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VOLUME X

BIBLIOTHÈQUES DE L'UNIVERSITÉ DE PARIS
ORSAY

ITHACA, N. Y.
THE EDITORS

LEIPZIG; BERNH. LIEBISCH (K. F. Koehler's Antiquarium)
for the continent of Europe

1906

ANNEXE

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ORSAY
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MOLECULAR ATTRACTION. V. AN APPLICATION OF THE THEORY TO TEN ADDITIONAL SUBSTANCES

BY J. E. MILLS

Introduction

In previous papers[1] we derived and discussed the equation,

$$1. \qquad \frac{L - E_1}{\sqrt[3]{d} - \sqrt[3]{D}} = \text{constant} = \mu'.$$

Here L is heat of vaporization of a liquid, E_1 is the energy spent in overcoming external pressure, $L - E_1$ is, therefore, the internal heat of vaporization, d and D are the density of liquid and vapor respectively, and the constant we have called μ'.

For a more complete discussion of the ideas underlying this equation and its limitations the reader is referred to the second paper to which reference is given above. It is sufficient to say here that the equation was deduced upon the assumption that the molecular attraction varied inversely as the square of the distance apart of the molecules. If the equation is proved true it will indicate that Newton's law of gravitation is applicable to the molecules of a liquid and that this law is of itself sufficient to explain the cohesion between the molecules of a liquid and the internal heat consumed in changing the liquid into a vapor.

In the second paper above cited the equation was applied to twenty-one substances, in most cases over a range of temperature extending from the freezing-point of the liquid nearly to the critical temperature itself, the excellent measurements of Drs. Ramsay and Young, and of Dr. Young being used. Except for the associated substances, to which the equation, *a priori*, could not have been supposed applicable, the constancy of the results given by the equation was excellent. When the variation of the constant from the mean value adopted was greater than two per-cent the cause of the divergence was examined more particularly both in that paper and in the two succeeding papers. These diver-

[1] Jour. Phys. Chem., 6, 209 (1902); 8, 383, 593 (1904); 9, 402 (1905).

gent values were shown usually to be caused by the great multiplication of errors of observation in the calculation. (Usually through the use of Biot's formula for the calculation of the $\frac{\partial P}{\partial T}$, a factor which was necessary for the calculation of the heat of vaporization thermodynamically.) Occasionally the nature of the substance rendered the observations at the temperature considered less accurate than usual. As a conclusion from the work of these papers, we believe that there can be no further doubt that ethyl oxide, di-isopropyl, isopentane, normal pentane, normal hexane, benzene, hexamethylene, fluo-benzene, chlor-benzene, brom-benzene, iodo-benzene, and carbon tetrachloride agree with the theory as closely as the experimental data will permit over the entire range of temperature examined, and even at the critical temperature itself.[1] Normal heptane, normal octane, and di-isobutyl show an unexplained divergence in the immediate neighborhood of the critical temperature. These substances having each given agreement with the theory over a very wide range of temperature it would seem that their divergence at the critical temperature (amounting in no case to ten percent from the mean constant and the entire variation from constancy extending in no case more than ten degrees), is more probably due to an increased inaccuracy in some one of the measurements entering into the calculation, or to some incipient change or decomposition taking place in the substance at this high temperature than to any inherent departure from the general law.

Stannic chloride was shown in the second paper to give a considerable unexplained divergence from the theory. But in that paper, Dr. Young, who made the measurements, is quoted (p. 402) as saying, "Stannic chloride spoils the surface of mercury even at low temperatures and special methods had to be used throughout. The accuracy is certainly not so great as with most of the other substances, but this will not, I think, explain the regular fall in the value of the constant." In the fourth paper, however, we again quoted (p. 407) Dr. Young as saying, "The observed values of the vapor pressure above 280°

[1] Jour. Phys. Chem., 9, 413 (1905).

C. for normal octane, stannic chloride, and acetic acid, are probably too low owing to an error in the temperature scale, etc.;" and showed that if correction were applied to the $\frac{\partial P}{\partial T}$ as outlined in that paper, stannic chloride also gave quite close agreement with the theory both at 280° C. and at the critical temperature, 318.7° C. We believe, therefore, that the agreement of stannic chloride with the theory is likewise as close as the accuracy of the observations will permit.

In the preceding papers we also showed that a number of other equations could be deduced from the principles under discussion and that these equations were similarly confirmed by the observations.

Summarizing, therefore, the work done on the non-associated substances, we believe that all of these examined, sixteen in number, and representing very large and various classes of compounds, agree substantially with the theory, and there is no divergence sufficiently pronounced to be regarded as distinct from the general rule.

The five associated substances examined gave an unexpectedly close agreement with the theory over a considerable range of temperature and we pointed out that this seemed to indicate that the molecular association in these cases was caused by the molecular attraction. Böttger, in a review of the second paper,[1] points out in evidence against this conclusion that water, as shown in that paper, gave a considerable divergence at the lower temperatures, 0° to 30° C. We are to blame for not having in that paper called attention to other measurements in part explanation of that divergence. This was through an oversight on our part. Dieterici from twenty experiments gave the value for the heat of vaporization of water at 0° C. as 596.8. Callendar gives the value as 593.5, and Griffiths, from seventy-three experiments, made with exceeding care, deduces the formula, $L = 596.73 - 0.6010\ T$. The work of Dieterici and Griffiths is, therefore, in practically perfect agreement and leaves no doubt that Regnault's values are too high at the lower temperatures.

[1] Jour. Am. Chem. Soc., 27, 309 (1905).

(The agreement between Griffiths and Regnault becomes closer with rise in temperature, at 100° C., both values being in accord to 0.04 of a calorie.) The density of the vapor used was dependent on Regnault's heat of vaporization, having been calculated from his measurements by Ramsay and Young.[1] Using Griffiths' value for the heat of vaporization and recalculating the density of the vapor therefrom and subsequently E_1, and substituting as before in Equation 1 above, we obtain:

WATER.

Temperature	Density of vapor	Latent heat	E_1	$L - E_1$	$\sqrt[3]{d} - \sqrt[3]{D}$	$\frac{L - E_1}{\sqrt[3]{d} - \sqrt[3]{D}}$
0° C.	$0.0_6 4814$	596.73	30.41	566.32	0.9830	576.1
10	$0.0_6 9328$	590.72	31.26	559.46	0.9789	571.5
20	$0.0_5 1721$	584.71	32.16	552.55	0.9736	567.5
30	$0.0_5 3034$	578.70	33.10	545.00	0.9674	563.4
	$\frac{\partial P}{\partial T}$					
240	438	429.5	47.8	381.7	0.6791	562.1
250	499	416.9	47.5	369.4	0.6586	561.0
260	566	402.5	46.8	355.7	0.6371	558.3
270	648	390.3	45.6	344.7	0.142	561.2

The value of the mechanical equivalent of heat used above in recalculating the density of the vapor was the value previously used by Ramsay and Young for their calculation. It is one-half of one percent lower than the value of Rowland as corrected by Day which we have used in these papers.

We made yet another error in trusting to the Biot formula given by Regnault for calculating the heat of vaporization at 240° to 270° C. The vapor-pressures calculated from this formula were up to 230° C. in splendid agreement with the values of the vapor-pressure experimentally determined by Ramsay and Young. But if the Regnault-Biot formula is forced beyond this point the divergence increases and becomes very marked. A new Biot formula could be calculated using the vapor pressures as given by Ramsay and Young throughout, but

[1] Phil. Trans., 183A, 115 (1892).

the calculation is laborious. Values quite sufficiently accurate for our purpose can be obtained by getting the $\frac{\partial P}{\partial T}$ for a considerable range of temperature directly from the observed vapor-pressures of Ramsay and Young and drawing a smoothed curve through these values plotted against the temperature and then reading from the curve. In this manner the values of the $\frac{\partial P}{\partial T}$ from 240° to 270° C. given above, were obtained. Using these values the latent heat was calculated and the values of the constant, μ', corrected as shown above. Changing the mean value formerly adopted from 556 to 558.4 we see that all values of the constant are within two percent of this mean value except at 0° C., which show a divergence of three and two-tenths percent, and at 10° C., which shows a divergence of a little over two percent. It seems to us quite possible that the explanation formerly given[1] will suffice to explain this divergence, especially when it is remembered that the mean value given is itself subject to some uncertainty.

But we wish to make it clear here that we have recorded these changes and corrections and pointed out the remaining source of error which it is impossible to correct only as a matter of fact. Personally we believe that the divergence of three and two-tenths percent above noted is yet greater than can be accounted for by the remaining sources of error. With associated substances we never expected the equation to yield a constant. But when the results over wide ranges of temperature proved *nearly constant* we thought it an indication that the association must be caused by the molecular attraction which we were considering. If this is true—if the molecular association is caused by this molecular attraction—we do not believe that the equation in its modified form would then yield an *exact* constant for these substances for the reason pointed out[2] when this suggestion was first made, *viz.*, the molecules could not be

[1] Jour. Phys. Chem., 8, 396 (1904).
[2] Ibid., 8, 402 (1904).

considered uniformly distributed throughout the space occupied by them—a supposition embraced in the formula.

We desire to make it clear exactly why we thought this *approach* to a constant value given by the equation indicated that the association was caused by the attraction under consideration. If the methods for measuring this molecular association are of any value, they indicate that the degree of association changes rather rapidly with a change in temperature. Now if this association is caused by some force other than the molecular force under consideration we would have as the temperature altered a continual and rapid change: in the nature of the substance under consideration; in the forces, at least two in number, acting between the different substances; in the number of molecules acting; and in the position of these molecular groups with respect to each other. Besides all of these changes, it must be remembered that, if analogy is worth anything, and in this case we believe that it is, the kinetic translational energy of the molecules as well as their internal energy must change with every change in the complexity of the molecule. For any considerable change in the complexity of the molecules the energy changes above noted would be very large and it seemed impossible to us that these various energy changes should so cancel as to leave the net result of the equation even nearly a constant. On the other hand, if the molecular association is caused by the molecular attraction under consideration, a change in the complexity of the molecules changes nothing but their distance apart. But the distance apart of the molecules is not regular as in the case of non-associated substances, but irregular, as we have to consider both the distance between groups of molecules and between the molecules of a group. We were not able to follow—have not, in fact, attempted to follow—the change this would necessitate in the equation given. (We think, however, that the effect would be to cause the constant given by the equation to increase with increasing molecular complexity, for the reason, briefly, that molecular association tends to draw the molecules, independently considered, on the average, closer together. This nearness would result in an apparently increased

attraction, *i. e.*, would cause the constant of attraction, μ', to show an increase in value.) But quite conceivably the change required in the equation would not be great. When, therefore, we found the value given by the equation for the associated substances surprisingly constant, and since these same associated substances showed a much larger absolute attraction, μ, than the non-associated substances, the conclusion that the association was caused by the attraction was suggested as a probable causal explanation of the two facts.

Another point has several times been brought to our attention. Because we have used in these papers the terms "molecule" and "molecular attraction" and "distance between the molecules," we do not possess the idea that a molecule is necessarily a little, hard sphere, or some other particular shape of a piece of matter. For our part, in the present part of this discussion we do not care to consider the nature of a molecule. We do not care whether it consists wholly of matter, or wholly of energy, or is a judicious mixture of the two. The law of gravitation has been shown to hold between large masses of matter. If later it happens to be proved that matter is not reality and that only energy exists, we do not suppose that the proof will greatly affect the calculations of the astronomers, or the position of the heavenly bodies or their movement in accordance with the law of gravitation. The object of this series of papers is to show that this same law of attraction exists between smaller masses of the same material of which these larger bodies are more conspicuous representatives. Following considerable precedent we have called these "smaller masses," "molecules," a term which conveys to every scientist, however broad-minded, a group of properties sufficiently clearly defined for the purpose in view. By the expression "distance between the molecules," we mean the distance between their centers of mass—an expression exactly analogous to the distance between two heavenly bodies. The expression "center of mass" is used only to designate a reality and those who have grasped the reality can use any nomenclature for its representation that is more pleasing to them.

Whatever opinion we ourselves hold as to the ultimate nature of the group of properties represented by the term molecule rests on grounds that are too insecure to make discussion of these views at this stage profitable. We only wish to emphasize that one may hold *any view* as to the ultimate constitution of matter and yet pursue an investigation of this character.

In this paper we consider the ten substances, methyl formate, ethyl formate, methyl acetate, chloroform, acetone, carbon disulphide, ammonia, carbon dioxide, nitrous oxide, and sulphur dioxide. Some of these substances were discussed, but inadequately, in the first paper. The details of the measurements used are given below. We may say here that when choice between the measurements of different observers was possible, it was not possible that the choice of the author could have been influenced unconsciously by any prejudice in favor of the theory, for in every case the measurements were chosen before any inkling of their possible bearing on the theory was obtained.

Constants for Biot's Formula

Before the heats of vaporization of methyl formate, ethyl formate, methyl acetate and sulphur dioxide could be calculated thermodynamically, it was necessary to have some means for obtaining the $\frac{\partial P}{\partial T}$ and, as usual, Biot's formula for vapor-pressure was used. The constants for this formula for ethyl formate and methyl acetate were kindly sent me by Dr. Young. They have never been published and so are given below. Dr. Young also sent the details of the method used in making the calculations and with this aid the constants for methyl formate and for sulphur dioxide were calculated and are likewise given below. For sulphur dioxide the vapor-pressures used as a basis were those given by Pictet, —30° to 50° C, inclusive, and Sajotschewsky, 60° to 156° C. The pressure at 110° given as observed was read from a curve through these results. Other observations on the vapor-pressure consulted were those of Faraday, —17.8° to 37.8°; Blümcke, —19.5° to 98.2°; and Regnault, —30° to 65° C. The measurements of Pictet and Regnault are in fair accord.

We give below the constants for these substances for use in a Biot formula of the form

2. $$\text{Log } \theta = a + b\,\alpha^l + c\,\beta^l.$$

We also give in Tables 1 and 2 the observed and calculated pressure and the difference between the calculated and observed pressures. While apparently it would have been possible by a recalculation to have improved somewhat the constants in the case of sulphur dioxide, the improvement would have been but slight and more apparent than real when other observations of the vapor-pressure of this substance were considered.

Ethyl formate:

$a = 7.163599$	
$b = -4.093017$	$\log b = 0.6120435$
$c = -1.452082$	$-\log c = 0.1619911$
$\log \alpha = \bar{1}.99915256$	
$\log \beta = \bar{1}.99482412$	
$l = t^\circ\,\text{C} + 10$	

Methyl acetate:

$a = 11.104596$	
$b = -7.692137$	$-\log b = 0.8860470$
$c = -1.866459$	$-\log c = 0.2710185$
$\log \alpha = \bar{1}.99967889$	
$\log \beta = \bar{1}.99531269$	
$l = t^\circ\,\text{C} + 10$	

Methyl formate:

$a = 6.2978414$	
$b = -3.34743$	$-\log b = 0.5247111$
$c = -0.457651$	$-\log c = \bar{1}.6605342$
$\log \alpha = \bar{1}.9984699$	
$\log \beta = \bar{1}.992553778$	
$l = t^\circ\,\text{C} - 10$	

Sulphur dioxide:

$a = 5.3926613$	
$b = 0.00087634$	$\log b = 4.9426748$
$c = -2.512724$	$-\log c = 0.4001448$
$\log \alpha = 0.01236576$	
$\log \beta = \bar{1}.99668639$	

TABLE I

Temperature	Methyl Acetate: Pressure calculated	Methyl Acetate: Pressure observed	Methyl Acetate: Δ	Ethyl Formate: Pressure calculated	Ethyl Formate: Pressure observed	Ethyl Formate: Δ
—20°C	18.89	19.05	— 0.16	22.60	22.49	0.11
—10	35.15	35.15	0.00	41.54	41.50	0.04
0	62.18	62.10	0.08	72.57	72.44	0.13
10	105.02	104.85	0.17	121.10	120.35	0.75
20	170.22	169.80	0.42	193.95	192.55	1.40
30	265.80	265.75	0.05	299.50	297.50	2.00
40	401.40	400.4	1.00	447.55	446.70	0.85
50	588.18	588.15	0.03	649.4	649.4	0.0
60	838.80	837.5	1.30	917.6	921.5	— 3.9
70	1167.2	—	—	1266.2	—	—
80	1588.9	1585	3.9	1710.1	1706	4.1
90	2120.3	2114	6.3	2265.7	2265	0.7
100	2779.1	2778	1.1	2949.9	2950	— 0.1
110	3584.4	3584	— 0.4	3781.0	3782	— 1.0
120	4555.8	4556	— 0.2	4777.7	4778	— 0.3
130	5714.5	5725	—10.5	5959.9	5954	5.9
140	7082.9	7100	—17.1	7348.4	7360	— 11.6
150	8684.8	8702	—17.2	8964.2	8954	10.2
160	10545	10566	—21	10830	10847	— 17
170	12691	12692	— 1	12969	12963	6
180	15152	15118	34	15405	15358	47
190	17960	17941	19	18164	18052	112
200	21146	21085	61	21271	21148	123
210	24737	24649	88	24754	24601	153
220	28804	28705	99	28640	28527	113
230	33360	33358	2	32961	32968	— 7
233.7	35180	35212	—32	—	—	—
235.3	—	—	—	35436	35535	— 99

TABLE 2

	Methyl Formate			Sulphur Dioxide		
Temperature	Pressure calculated	Pressure observed	Δ	Pressure calculated	Pressure observed	Δ
—20° C	64.83	67.7	—2.87			
—10	115.13	117.65	—2.52	760.0	760.0	0.0
0	193.71	195.0	—1.29	1163.3	1147.6	15.7
10	311.00	309.4	1.60	1726.2	1786.0	—59.8
20	479.47	476.4	3.07	2489.3	2508.0	—18.7
30	713.48	707.9	5.58	3496.0	3496.0	0.0
40	1029.3	1029.0	0.3	4791.7	4712.0	79.7
50	1445.1	1452.0	—6.9	6423.1	6308.0	115.1
60	1981.0	1991.0	—10.0	8435.9	8428.4	7.5
70	2658.6	2673	—14.4	10875.4	10875.6	—0.2
80	3501.3	3508	— 6.7	13789	13748	41
90	4534.2	4524	10.2	17225	17077	148
100	5783.8	5774	9.8	21242	21143	99
110	7278.0	7278	0.0	25916	25916	0.0
120	9046.2	9016	30.2	31351	31586	—235
130	11119	11105	14	37705	—	—
140	13527	13570	—43	45225	—	—
145	—	—	—	49536	—	—
150	16303	16330	—27	54302	54302	0.0
156	—	—	—	60747	59964	78.3
160	19479	19500	—21			
170	23089	23015	74			
180	27163	27040	123			
190	31736	31550	186			
200	36839	36685	154			
206	40168	40085	83			
210	42502	42510	— 8			
212	43704	43755	—51			
213	44315	44410	—95			
213.5	44622	44670	—48			
214	44932	45030	—98			

The Measurements

The complete measurements used are given in the Tables 4 to 14, inclusive. The references and other details concerning the measurements are given below. v and V represent the volume of liquid and vapor respectively. T represents temperature; P, pressure; m, molecular weight.

Below when reference to the original publication of the author is not given, the data can be obtained from the Physikalisch-Chemische Tabellen of Landolt and Börnstein. The data bearing on the substances under consideration that is recorded in Dammer's "Anorganische Chemie," in Beilstein, in the Physical Chemical Tables of Landolt and Börnstein and Castell-Evans, in Clarke's Table of Specific Gravities, as well as that in other works and journals coming under the author's observation were consulted. When in doubt as to the most accurate measurements, a decision was usually reached by plotting all of the measurements and drawing a smoothed curve through them. The data quoted as from Peabody's Tables on the Properties of Steam are usually taken by that author from Zeuner's Mechanische Wärmetheorie with slight changes. Zeuner in his calculations used mainly the measurements given by Regnault.

We also give below the value for A where A is used in calculating the heat of vaporization and is given by the equation

3. $$A = 168.775\ (b \log \alpha_1\alpha' + c \log \beta_1\beta');$$

and L by the equation,

4. $$L = \frac{P, \Delta v, T}{10^6} A.$$

Where the density of the vapor was calculated we used for the calculation the equation,

5. $$D = 0.0_4 16014 \frac{Pm}{T}.$$

Where E_1 is calculated we used the formula,

6. $$E_1 = 0.0_4 31833\ P(V - v).$$

Methyl Formate.—The measurements used were given by Young,[1] except the vapor density at 0° C, which was calculated. The molecular weight used was taken as 60.032. The pressures used were taken as above noted from Biot's formula based on Young's measurements.

$A = \text{antilog } (\bar{1}.9367391 - 0.0015301t) + \text{antilog } (\bar{1}.7597784 - 0.00744622 2t)$, $t = t°\text{ C} - 10$.

Ethyl Formate.—Data given by Young.[1] The vapor-density at 0° C was calculated, the molecular weight being taken as 74.05. The vapor pressures used were taken from the Biot formula above described.

$A = \text{antilog } (\bar{1}.7674599 - 0.00084744t) + \text{antilog } (0.1032834 - 0.00517588t)$, $t = t°\text{ C} + 10$.

Methyl Acetate.—Data given by Young.[1] The vapor-density at 0° C was calculated, the molecular weight being taken as 74.05. The vapor pressures used were taken from the Biot formula as above described.

$A = \text{antilog } (\bar{1}.6200090 - 0.00032111t) + \text{antilog } (0.1692504 - 0.00468731t)$, $t = t°\text{ C} + 10$.

Chloroform.—The pressure and density of the vapor, the heat of vaporization, E_n, and $L - E_n$, are taken from the tables on the Properties of Steam by C. H. Peabody. The density of the liquid from 0° to 60° C is taken from Thorpe,[2] and at 100° C the value was obtained by extending Thorpe's formula. The latter proceeding is open to objection, but in this case can hardly introduce serious error, the variation in the density of a liquid at low vapor-pressures being usually of a nearly uniformly varying increment. The molecular weight was taken as 119.358.

Acetone—The pressure and density of the vapor, the heat of vaporization, E_n, and $L - E_n$, are from Peabody's Tables. The density of the liquid, 0° to 60° C inclusive is from Thorpe,[3]

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[1] Jour. Chem. Soc., 53, 1191 (1893).
[2] Ibid., 37, 197 (1880).
[3] Ibid., 37, 212 (1880).

and, as in the case of chloroform, his formula was extended to 100° C. The molecular weight was taken as 58.048.

Carbon Disulphide.—The vapor-pressures given follow Ramsay and Young's measurements from 0° to 120° inclusive, then Regnault's values are used. The density of the vapor is taken from Peabody's Tables. The heat of vaporization, E_1, and $L - E_1$, are likewise taken from Peabody's Tables. These are based on Regnault's values of the vapor-pressure but these values are in good accord with the measurements of Ramsay and Young. The density of the liquid is from Thorpe, 0° to 50° inclusive, and then from 60° to 160° C Hirn's formula is used, the value at 0° as given by Thorpe being used as a basis for that formula.[1] The molecular weight is taken as 76.14.

Ammonia.—The vapor-pressures follow Regnault. The densities of the liquid follow D'Andreef, —10° to 20° C inclusive, the other values being interpolated from D'Andreef's results. The density of the vapor and the heats of vaporization are from the formulas given in Peabody's Tables. E_1 is calculated according to Equation 6 above. The molecular weight is taken as 17.064. The data on ammonia is not so trustworthy as are the measurements on the substances hitherto mentioned.

Carbon Dioxide.—The pressures of carbon dioxide, —20° to 25° C inclusive, are from Regnault. The value at —30° was taken from a curve connecting the observations of Regnault, —20° to 30°, and Cailletet, —80° to —40°. The value at 30° agrees with the critical pressures adopted, the latter being the value given by Amagat. The vapor-pressures of carbon dioxide are not very accurately known and the values as given may be subject to considerable error. The density of the liquid at 30° is from Thilorier. (See Clarke's Specific Gravities, p. 43.) The value at the critical point is from Amagat. The other values of the density of this liquid were obtained from a smooth curve drawn through the data of Cailletet and Mathias. The densities of the vapor and the heats of vaporization are from a smooth curve through measurements given by

[1] Jour. Chem. Soc., 37, 363 (1880).

Cailletet and Mathias and Mathias. See thesis by Mathias "Sur la Chaleur de Vaporisation des Gas Liquefiés." Note also determinations of the heat of vaporization by Chappuis and by Regnault. The molecular weight used is 44.00. E_1 is calculated using Equation 6 above.

Nitrous Oxide.—The vapor-pressures are from Regnault as given in Dammer's Anorganische Chemie. The density of the vapor is from a curve following values as given by Cailletet and Mathias. The density of the liquid is from a curve following the values given by Villard, and Cailletet and Mathias as given in Clarke's Tables of Specific Gravities. The heat of vaporization, —25° to 0° C inclusive, is taken from the thesis of E. Mathias above mentioned. The values of these measurements quoted in many tables are incorrect. The heat of vaporization from 0° to 30° C is from measurements by Mathias and is taken from thesis by him. E_1 is calculated by Equation 6 given above. The molecular weight is taken as 44.08.

Sulphur Dioxide.—Two tables, 13 and 14, are used in discussing the data for sulphur dioxide. In Table 13 the vapor-pressures are the values as given by Pictet, except at 60° C where the value is from Sajotschewsky's measurements. In Table 14 the vapor-pressures are from Biot's formula calculated as hitherto noted in this paper. The values for the density of liquid and vapor are the same in both tables and are taken from a curve drawn through the values given by Cailletet and Mathias, except the density of the vapor at —10° C, which is calculated. The molecular weight is taken as 64.07. The values of the density of the liquid given by D'Andreef are in good agreement with the corresponding measurements of Cailletet and Mathias. The heats of vaporization used in the first table are taken from the thesis above mentioned by Mathias, p. 49, except at 10° C where the value is from Estreicher.[1] The heats of vaporization in the second table are calculated thermodynamically using Equations 2, 3 and 4, above.

$A = \text{antilog}\ (\bar{3}.2622041 - 0.01236576l) + \text{antilog}\ (0.1477544 - 0.00331361l)$, where $l = t°, C + 10$.

[1] Zeit. phys. Chem., 49, 597 (1904).

E_1 is calculated in each table according to Equation 6.

The Calculations and Results

The calculations involved were all checked and carried to that degree of accuracy warranted by the measurements.

We have already critically discussed[1] the extent to which errors of observation occurring in the various measurements used will affect the value of the constant given by the ratio, $\frac{L - E_1}{\sqrt[3]{d} - \sqrt[3]{D}}$. From that discussion, we conclude that since the errors of measurement were always compounded and were often multiplied in their proportionate effect upon the constant, that a divergence from the mean values of the constant of less than two percent could be regarded as within the limit of error of observation, even when using Table 3 measurements that had been most carefully carried out. The mean value for the constant which we have called μ', adopted for the various substances, is given in Table 3. In the tables all values that differ from these mean values by more than two percent are marked with an asterisk. We give in Table 3 a summary of the values of μ'.

It will be seen that the three esters give excellent agreement with the theory until the critical temperature is approached. The increased errors in the neighborhood of the critical temperature we have already shown to be due to the use of Biot's formula in calculating the $\frac{\partial P}{\partial T}$. It was shown in the fourth paper already cited that Biot's formula cannot be made exactly to fit the observations in the immediate neighborhood of the critical temperature and that the discrepancy, although slight when the vapor-pressure is considered, becomes proportionately so great when the $\frac{\partial P}{\partial T}$ is considered, as to be the cause of a very considerable error in the calculation of that quantity. We also showed (p. 413, Table III) in that paper, that if the proper correction were applied to the $\frac{\partial P}{\partial T}$ the values of μ' for these three esters became

[1] Jour. Phys. Chem., 8, 392, etc. (1904)

TABLE 3

Temperature	Methyl formate	Ethyl formate	Methyl acetate	Chloro-form	Acetone	Carbon disulphide	Ammo-nia	Carbon dioxide	Nitrous oxide	Sulphur dioxide	
Mean value	121.5	107.2	109.0	57.97	150.8	82.41	381.9	95.16	83.70	85.80	85.80
—30° C							381.3	94.58			
—20							380.9	96.28	82.51		
—10							380.6	95.85	86.99*	88.57*	87.36
0	123.9	108.8	110.7	58.02	150.8	82.22	380.5	95.38	90.74*	87.02*	86.79
10				57.90	150.7	82.38	381.1	93.71	90.48*	85.51	84.20
20				57.80	150.7	82.52	382.2	90.46*	84.90	84.31	84.10
30	125.6*			57.78	150.8	82.63	383.2	61.42*	62.48*	82.69*	84.42
40	124.6*			57.36	149.7	82.71	385.1			81.09*	84.63
50	122.5			57.89	151.1	82.80				80.14*	81.62*
60	121.2	108.8	110.8	58.02	151.2	82.85				77.76*	83.04*
70	120.5	108.3	110.8			82.85					85.78
80	119.1	108.4	110.5			82.82					88.15*
90	119.2	108.2	110.0			82.75					88.88*
100.	119.9	107.5	109.8	58.97	151.3	82.61					87.55*
110	120.0	107.3	109.4			82.46					86.57
120	120.2	107.2	109.1			82.23					87.65*
130	119.8	107.4	109.5			81.93					89.17*
140	119.8	107.3	109.6			81.63					91.36*
150	119.7	106.5	109.9			81.19					94.20*
155											96.00*
160	119.2	106.5	109.8								
170	119.1	106.0	109.5								
180	118.1*	106.4	108.8								
190	116.4*	106.0	108.5								
200	113.3*	105.1	108.2								
210	106.6*	103.8*	107.0								
213.5	101.2*										
220		101.3*	105.0*								
230		97.6*	100.4*								
233			96.6*								
234		94.0*									
Critical temperature	214.0°	235.3°	233.7°	260.0°	237.5°	277.7°	131.0°	31.35°	39.0°	156.0°	156.0°

much nearer the mean values. The corrected values of μ' for the highest temperatures of observation and for the critical temperature are shown below.

	Temperature	μ'	Critical temperature	μ'
Methyl formate, ...	213.5°	120.1	214.0°	119.8
Ethyl formate, ...	234°	104.4	235.3°	103.9
Methyl acetate, ...	235°	103.8	233.7°	103.6

The corrected values for methyl formate are therefore in accord with the theory. Ethyl formate is, at the critical temperature, still three percent from the mean value of the constant, but this divergence is accounted for by the fact that it decomposes slightly at this high temperature. We know of no reason for the unusually large error, 5.5 percent, still shown by the corrected value for methyl acetate. It will be recalled that di-isobutyl, normal heptane, and normal octane showed a similar divergence.

The divergence of methyl formate at 30° and 40° we consider probably due to an error in the density of the vapor, that determination being less accurate at the low temperatures. In confirmation of this conclusion we would call attention to the irregularity of the PV curve when plotted against the temperature. The usual form of this curve was shown in the third paper. We show the values of PV in Table 15.

Of the other substances, chloroform, acetone, carbon disulphide, and ammonia give values in excellent agreement with the mean values adopted for the constants throughout the entire range of temperature for which each substance was examined. Acetone and ammonia are probably associated liquids, and if the range of temperature examined were greater we would expect to find a divergence from the mean value for these substances.

Carbon dioxide shows a very marked decrease in the value of the constant as the critical temperature is approached. But large as is this variation, it is not larger than the probable error

of the observations as they affect the constant, for not only are the observations a matter of increasing difficulty at the high temperatures, but also, owing to the fact that both numerator and denominator of the fraction, $\frac{L_t - E_1}{\sqrt[3]{d} - \sqrt[3]{D}}$, diminish rapidly as the critical temperature is approached, the errors of observation are multiplied in their effect upon the constant. Thus while the absolute error in the determination of the heat of vaporization is likely to be as large as 30° as it is at —30° C, the effect on the constant of such an absolute error is seven times as great. Almost a similar statement will apply to the effect of the errors of observation upon the densities of liquid and vapor.

For nitrous oxide the statements made above for carbon dioxide will apply, and in addition thereto we would point out that the heats of vaporization at the lower temperatures, —25° to 10° C inclusive, are from the measurements of Cailletet and Mathias and the remaining values are from the measurements of Mathias, and that these two sets of measurements overlap at 0° C where they show a divergence of two percent, a divergence which would be somewhat increased in its effect upon the constant. More than this, the value for the critical temperature given by Mathias was 35° C, whereas the value given in Travers' Experimental Study of Gases is 39° C and indicates, that if the value is true the observations we used could not have been accurate as the critical temperature was approached. Since, as above pointed out, such an error would be greatly multiplied in its proportionate effect upon the constant, μ', it is quite possible that the divergence of both nitrous oxide and carbon dioxide is only apparent.

With sulphur dioxide the case is different. At 60° C the errors of observation are not greatly enlarged in their effect upon the constant and while the data used was considered less accurate than usual, it did not seem reasonable to lay the divergence entirely upon the measurements. It was possible in this case, however, using the data at hand, to calculate the heats of vaporization thermodynamically. This was done and the results are given in Table 14. While the divergence from the theory is yet considerable it occurs mainly at the higher temperatures where the measurements are less accurate.

TABLE 4
Methyl Formate

Temperature	Pressure	Density of liquid	Density of vapor	$\frac{\rho \Delta V_1 T}{10^6}$	A	Latent heat	E_1	$L - E_1$	$\sqrt[3]{d} - \sqrt[3]{D}$	$\frac{L - E_1}{\sqrt[3]{d} - \sqrt[3]{D}}$
0°C.	193.71	1.0032	0.0_36821	77.45	1.57817	122.23	9.03	113.20	0.9136	123.9
30	713.48	0.9598	0.002225	96.96	1.21381	117.68	10.19	107.49	0.8559	125.6*
40	1029.3	0.9447	0.003150	101.92	1.12161	114.31	10.36	103.95	0.8346	124.6*
50	1445.1	0.9294	0.004396	105.65	1.04051	109.92	10.41	99.51	0.8121	122.5
60	1981.0	0.9133	0.005988	109.46	0.96887	106.05	10.46	95.59	0.7886	121.2
70	2658.6	0.8968	0.007968	113.43	0.90532	102.69	10.53	92.16	0.7646	120.5
80	3501.3	0.8803	0.01052	116.06	0.84871	98.50	10.47	88.03	0.7393	119.1
90	4534.2	0.8634	0.01352	119.79	0.79804	95.60	10.50	85.10	0.7140	119.2
100	5783.8	0.8452	0.01711	123.57	0.75247	92.98	10.55	82.43	0.6878	119.9
110	7278.0	0.8264	0.02153	126.09	0.71131	89.69	10.48	79.21	0.6602	120.0
120	9046.2	0.8070	0.02685	128.03	0.67396	86.29	10.37	75.92	0.6316	120.2
130	11119	0.7860	0.03344	128.27	0.63990	82.08	10.13	71.95	0.6007	119.8
140	13527	0.7638	0.04124	128.11	0.60871	77.97	9.87	68.10	0.5686	119.8
150	16303	0.7403	0.05063	126.86	0.58003	73.58	9.55	64.03	0.5347	119.7
160	19479	0.7136	0.06231	123.50	0.55353	68.36	9.08	59.28	0.4971	119.2
170	23089	0.6844	0.07634	119.03	0.52897	62.96	8.55	54.41	0.4571	119.1
180	27163	0.6521	0.09434	111.61	0.50610	56.48	7.84	48.64	0.4120	118.1*
190	31736	0.6148	0.1178	100.79	0.48475	48.86	6.93	41.93	0.3601	116.4*
200	36839	0.5658	0.1524	83.48	0.46474	38.80	5.62	33.18	0.2929	113.3*
206	40168	0.5241	0.1862	66.58	0.45332	30.18	4.42	25.76	0.2353	109.5*
210	42502	0.4857	0.2188	51.54	0.44593	22.98	3.40	19.58	0.1835	106.6*
212	43704	0.4549	0.2451	39.85	0.44230	17.63	2.62	15.01	0.1433	104.8*
213	44315	0.4328	0.2681	30.58	0.44050	13.47	2.00	11.47	0.1116	102.8*
213.5	44622	0.4157	0.2865	23.53	0.43961	10.34	1.54	8.80	0.0870	101.2*

TABLE 5
Ethyl Formate

Temperature	Pressure	Density of liquid	Density of vapor	$\frac{p_1 \Delta V.T}{10^6}$	A	Latent heat	E_1	$L - E_1$	$\sqrt[3]{d} - \sqrt[3]{D}$	$\frac{L - E_1}{\sqrt[3]{d} - \sqrt[3]{D}}$
0° C	72.57	0.9480	$0.0_3 3152$	62.84	1.70006	106.83	7.33	99.50	0.9143	108.8
60	917.6	0.8689	0.003356	90.68	1.06144	96.25	8.69	87.56	0.8045	108.8
70	1266.2	0.8552	0.004566	94.56	0.98968	93.59	8.78	84.81	0.7833	108.3
80	1710.1	0.8409	0.006061	98.87	0.92509	91.46	8.92	82.54	0.7616	108.4
90	2265.7	0.8262	0.007937	102.62	0.86684	88.95	9.00	79.95	0.7389	108.2
100	2949.9	0.8112	0.01031	105.41	0.81426	85.83	9.00	76.83	0.7150	107.5
110	3781.0	0.7955	0.01312	108.47	0.76671	83.16	9.02	74.14	0.6907	107.3
120	4777.7	0.7796	0.01656	110.99	0.72366	80.32	8.99	71.33	0.6655	107.2
130	5959.9	0.7628	0.02062	113.36	0.68461	77.60	8.95	68.65	0.6395	107.4
140	7348.4	0.7448	0.02558	114.73	0.64914	74.47	8.84	65.63	0.6119	107.3
150	8964.2	0.7257	0.03164	114.50	0.61685	70.63	8.62	62.01	0.5823	106.5
160	10830	0.7058	0.03876	114.44	0.58735	67.21	8.41	58.80	0.5520	106.5
170	12969	0.6843	0.04739	112.61	0.56048	63.12	8.09	55.03	0.5193	106.0
180	15405	0.6610	0.05747	110.94	0.53584	59.44	7.80	51.64	0.4852	106.4
190	18164	0.6355	0.07018	106.63	0.51323	54.72	7.33	47.39	0.4473	106.0
200	21271	0.6066	0.08621	100.08	0.49244	49.28	6.74	42.54	0.4047	105.1
210	24754	0.5724	0.1073	90.51	0.47326	42.83	5.97	36.86	0.3551	103.8
220	28640	0.5290	0.1379	75.67	0.45553	34.47	4.88	29.59	0.2921	101.3
225	30745	0.5014	0.1587	65.99	0.44717	29.51	4.21	25.30	0.2530	100.0
230	32961	0.4635	0.1890	51.91	0.43912	22.79	3.28	19.51	0.2000	97.6
233	34346	0.4281	0.2198	38.40	0.43443	16.68	2.41	14.27	0.1502	95.0
234	34817	0.4117	0.2353	32.14	0.43289	13.91	2.02	11.89	0.1265	94.0

TABLE 6
Methyl Acetate

Temperature	Pressure	Density of liquid	Density of vapor	$\frac{p_1 \Delta V_1 T}{10^6}$	A	Latent heat	E_1	$L - E_1$	$\sqrt[3]{d} - \sqrt[3]{D}$	$\frac{L - E_1}{\sqrt[3]{d} - \sqrt[3]{D}}$
0°C.	62.18	0.9593	$0.0_3 2700$	62.87	1.73931	109.34	7.33	102.01	0.9216	110.7
60	838.80	0.8800	0.003072	90.61	1.08950	98.71	8.66	90.05	0.8129	110.8
70	1167.2	0.8662	0.004184	95.15	1.01561	96.62	8.83	87.79	0.7921	110.8
80	1588.9	0.8519	0.005618	99.12	0.94902	94.07	8.94	85.13	0.7702	110.5
90	2120.3	0.8374	0.007435	102.59	0.88896	91.19	9.00	82.19	0.7474	110.0
100	2779.1	0.8221	0.009662	106.00	0.83476	88.48	9.05	79.43	0.7238	109.8
110	3584.4	0.8060	0.01242	108.85	0.78585	85.53	9.05	76.48	0.6990	109.4
120	4555.8	0.7893	0.01577	111.18	0.74167	82.46	9.00	73.46	0.6734	109.1
130	5714.5	0.7715	0.01972	113.77	0.70175	79.83	8.99	70.84	0.6470	109.5
140	7082.9	0.7532	0.02457	115.27	0.66564	76.73	8.88	67.85	0.6192	109.6
150	8684.8	0.7339	0.03026	116.40	0.63296	73.68	8.76	64.92	0.5904	109.9
160	10545	0.7133	0.03731	115.95	0.60337	69.96	8.53	61.43	0.5593	109.8
170	12691	0.6907	0.04598	114.11	0.57654	65.79	8.20	57.59	0.5257	109.5
180	15152	0.6671	0.05682	110.48	0.55220	61.00	7.77	53.23	0.4894	108.8
190	17960	0.6410	0.06993	105.93	0.53010	56.14	7.28	48.86	0.4502	108.5
200	21146	0.6100	0.08658	99.14	0.51000	50.56	6.67	43.89	0.4057	108.2
210	24737	0.5741	0.1091	88.77	0.49172	43.65	5.85	37.80	0.3532	107.0
220	28804	0.5281	0.1416	73.40	0.47505	34.87	4.74	30.13	0.2870	105.0*
227	31937	0.4818	0.1776	56.85	0.46425	26.39	3.62	22.77	0.2218	102.6*
230	33360	0.4527	0.2028	45.64	0.45984	20.99	2.89	18.10	0.1802	100.4*
232	34334	0.4226	0.2288	34.68	0.45695	15.85	2.18	13.67	0.1388	98.5*
233	34829	0.3995	0.2525	25.73	0.45553	11.70	1.62	10.08	0.1044	96.6*

TABLE 7

Chloroform

Temperature	Pressure	Density of liquid	Density of vapor	Latent heat	E_1	$L - E_1$	$\sqrt[4]{d} - \sqrt[4]{D}$	$\frac{L - E_1}{\sqrt[4]{d} - \sqrt[4]{D}}$
0°C.	59.72	1.5264	0.0_34207	67.00	4.55	62.45	1.0764	58.02
10	100.47	1.5074	0.0_36780	66.04	4.75	61.29	1.0586	57.90
20	160.47	1.4885	0.001042	65.08	4.94	60.14	1.0404	57.80
30	247.51	1.4697	0.001554	64.10	5.10	59.00	1.0212	57.78
40	369.26	1.4503	0.002248	63.13	5.26	57.87	1.0009	57.36
50	535.05	1.4308	0.003170	62.13	5.40	56.73	0.9799	57.89
60	755.44	1.4108	0.004356	61.13	5.53	55.60	0.9583	58.02
100	2428.5	1.3291	0.01287	57.01	6.00	51.01	0.8650	58.97

TABLE 8

Acetone

Temperature	Pressure	Density of liquid	Density of vapor	Latent heat	E_1	$L - E_1$	$\sqrt[4]{d} - \sqrt[4]{D}$	$\frac{L - E_1}{\sqrt[4]{d} - \sqrt[4]{D}}$
0°C.	63.33	0.8186	0.0_32339	140.50	8.68	131.82	0.8738	150.8
10	110.32	0.8074	0.0_33723	139.01	9.50	129.51	0.8593	150.7
20	197.9	0.7960	0.0_35688	137.33	10.17	127.16	0.8439	150.7
30	281.0	0.7846	0.0_38425	135.48	10.65	124.83	0.8279	150.8
40	420.2	0.7731	0.001215	133.44	11.05	121.39	0.8111	149.7
50	602.9	0.7614	0.001715	131.22	11.36	119.86	0.7934	151.1
60	860.5	0.7497	0.002372	128.82	11.60	117.22	0.7750	151.2
100	2797	0.7025	0.007289	117.37	12.20	105.17	0.6951	151.3

TABLE 9
Carbon Disulphide

Temperature	Pressure	Density of liquid	Density of vapor	Latent heat	E_1	$L - E_1$	$\sqrt[3]{d} - \sqrt[3]{D}$	$\frac{L - E_1}{\sqrt[3]{d} - \sqrt[3]{D}}$
0°C.	131.98	1.2921	0.0_35662	90.00	7.24	82.76	1.0065	82.22
10	203.0	1.2775	0.0_38496	89.06	7.48	81.58	0.9903	82.38
20	301.8	1.2625	0.001239	88.02	7.71	80.31	0.9734	82.52
30	437.0	1.2473	0.001759	86.88	7.91	78.97	0.9557	82.63
40	617.0	1.2321	0.002440	85.64	8.10	77.54	0.9375	82.71
50	856.7	1.2164	0.003315	84.31	8.27	76.04	0.9184	82.80
60	1164	1.2003	0.004417	82.87	8.42	74.45	0.8986	82.85
70	1552	1.1844	0.005794	81.34	8.56	72.78	0.8784	82.85
80	2034	1.1684	0.007473	79.70	8.67	71.03	0.8577	82.82
90	2622	1.1518	0.0095	77.97	8.77	69.20	0.8363	82.75
100	3330	1.1349	0.01195	76.14	8.85	67.29	0.8145	82.61
110	4167	1.1176	0.01484	74.21	8.90	65.31	0.7920	82.46
120	5145	1.0997	0.01821	72.18	8.94	63.24	0.7691	82.23
130	6292	1.0811	0.02212	70.05	8.96	61.09	0.7456	81.93
140	7604	1.0618	0.0267	67.83	8.95	58.88	0.7213	81.63
150	9096	1.0417	0.0318	65.50	8.92	56.58	0.6969	81.19

TABLE 10
Ammonia

Temperature	Pressure	Density of liquid	Density of vapor	Latent heat	E_1	$L - E_1$	$\sqrt[3]{d} - \sqrt[3]{D}$	$\frac{L - E_1}{\sqrt[3]{d} - \sqrt[3]{D}}$
—30° C	866.09	0.6760	0.001002	324.0	27.5	296.5	0.7775	381.3
—20	1392.1	0.6627	0.001568	316.0	28.2	287.8	0.7556	380.9
—10	2144.6	0.6492	0.002348	308.0	29.0	279.0	0.7330	380.6
0	3183.3	0.6364	0.003377	300.0	29.8	270.2	0.7102	380.5
10	4575.0	0.6230	0.004742	292.0	30.5	261.5	0.6861	381.1
20	6387.8	0.6089	0.006447	284.0	31.2	252.8	0.6615	382.2
30	8701.0	0.5960	0.008569	276.0	31.9	244.1	0.6370	383.2
40	11595.3	0.5830	0.01117	268.0	32.4	235.6	0.6118	385.1

TABLE 11
Carbon Dioxide

Temperature	Pressure	Density of liquid	Density of vapor	Latent heat	E_1	$L - E_1$	$\sqrt[4]{d} - \sqrt[4]{D}$	$\frac{L - E_1}{\sqrt[4]{d} - \sqrt[4]{D}}$
—30° C	10891	1.045	0.0340	75.2	9.86	65.34	0.6908	94.58
—20	15147	1.002	0.0525	69.0	8.70	60.30	0.6263	96.28
—10	20338	0.956	0.0725	62.7	8.25	54.45	0.5681	95.85
0	26904	0.905	0.0975	56.2	7.84	48.36	0.5070	95.38
10	34998	0.846	0.135	47.5	6.94	40.56	0.4328	93.71
20	44718	0.766	0.201	35.0	5.22	29.78	0.3292	90.46*
25	48716	0.705	0.253	26.0	3.93	22.07	0.2575	85.72*
30	53732	0.600	0.342	11.0	2.15	8.85	0.1441	61.42*

TABLE 12
Nitrous Oxide

Temperature	Pressure	Density of liquid	Density of vapor	Latent heat	E_1	$L - E_1$	$\sqrt[4]{d} - \sqrt[4]{D}$	$\frac{L - E_1}{\sqrt[4]{d} - \sqrt[4]{D}}$
—25° C	15695	1.018	0.0400	66.90	12.00	54.90	0.6640	82.68
—20	17587	1.000	0.0450	65.04	11.88	53.16	0.6443	82.51
—10	22008	0.962	0.0615	62.20	10.66	51.54	0.5925	86.99*
0	27421	0.910	0.082	58.2	9.68	48.52	0.5347	90.74*
10	34019	0.856	0.112	50.7	8.40	42.30	0.4675	90.48*
20	42028	0.782	0.152	40.0	7.09	32.91	0.3876	84.90
25	46641	0.737	0.181	32.7	6.18	26.52	0.3376	78.55*
30	51709	0.681	0.218	22.5	5.13	17.37	0.2780	62.48*

TABLE 13
Sulphur dioxide

Temperature	Pressure	Latent heat	E_1	$L - E_1$	$\sqrt[4]{d} - \sqrt[4]{D}$	$\frac{L - E_1}{\sqrt[4]{d} - \sqrt[4]{D}}$
—10° C	760.0	95.90	8.14	87.76	0.9908	88.57*
0	1147.6	91.87	8.09	83.78	0.9628	87.02
10	1786.0	88.00	8.32	79.68	0.9318	85.51
20	2508.0	84.05	8.17	75.88	0.9000	84.31
30	3496.0	80.04	8.22	71.82	0.8685	82.69*
40	4712.0	75.94	8.17	67.77	0.8357	81.09*
50	6308.0	71.82	7.87	63.95	0.7979	80.14*
60	8428.4	67.60	8.17	59.43	0.7643	77.76*

TABLE 14
Sulphur dioxide

Temperature	Pressure	Density of liquid	Density of vapor	$\frac{P_1 \Delta V_1 T}{10^6}$	A	Latent heat	E_1	$L - E_1$	$\sqrt[4]{d} - \sqrt[4]{D}$	$\frac{L - E_1}{\sqrt[4]{d} - \sqrt[4]{D}}$
—10° C	760.0	1.460	0.002964	67.294	1.4071	94.70	8.14	86.56	0.9908	87.36
0	1163.3	1.435	0.0045	70.350	1.3044	91.76	8.20	83.56	0.9628	86.79
10	1726.2	1.410	0.0068	71.512	1.2096	86.50	8.04	78.46	0.9318	84.20
20	2489.3	1.380	0.0097	74.686	1.1221	83.80	8.11	75.69	0.9000	84.10
30	3496.0	1.353	0.0134	78.295	1.0414	81.54	8.22	73.32	0.8685	84.42
40	4791.7	1.325	0.0181	81.724	0.96715	79.04	8.31	70.73	0.8357	84.63
50	6423.1	1.296	0.0250	81.329	0.89917	73.13	8.01	65.12	0.7979	81.62*
60	8435.9	1.266	0.0320	85.581	0.83718	71.65	8.18	63.47	0.7643	83.04*
70	10875.4	1.233	0.0396	91.169	0.78109	71.21	8.46	62.75	0.7315	85.78
80	13789	1.194	0.0488	95.628	0.73090	69.89	8.62	61.27	0.6955	88.15*
90	17225	1.158	0.0608	97.465	0.68676	66.93	8.55	58.38	0.6568	88.88*
100	21242	1.118	0.0777	94.928	0.64902	61.61	8.10	53.51	0.6112	87.55*
110	25916	1.070	0.0995	90.541	0.61823	55.97	7.54	48.43	0.5594	86.57
120	31351	1.018	0.1255	86.106	0.59527	51.26	6.97	44.29	0.5053	87.65*
130	37705	0.960	0.161	78.545	0.58138	45.66	6.20	39.46	0.4425	89.17*
140	45225	0.878	0.216	65.171	0.57836	37.69	5.02	32.67	0.3576	91.36*
145	49536	0.827	0.254	56.514	0.58164	32.87	4.30	28.57	0.3053	93.58*
150	54302	0.760	0.314	42.723	0.58862	25.15	3.21	21.94	0.2329	94.20*
155	59610	0.650	0.420	21.430	0.59973	12.85	1.59	11.26	0.1173	96.00*

Of the substances examined, therefore, seven, methyl formate, ethyl formate, methyl acetate, chloroform, acetone, ammonia, and carbon disulphide, have been found to give substantial agreement with the theory. Three substances, carbon dioxide, nitrous oxide, and sulphur dioxide, have shown considerable divergence, but a divergence that it would seem is quite probably to be attributed wholly to errors in the measurements used, the proportionate effect of these errors having been multiplied by the calculations involved.

On Crompton's Equation

We have in previous papers repeatedly called attention to an equation allowing the heat of vaporization to be calculated, proposed on theoretical grounds by Mr. H. Crompton. The equation may take the form:

7. $$L = \frac{9.154}{m} T \log \frac{d}{D} \text{ Cals.}$$

We give below, in Tables 15 to 24, in the columns headed "Crompton," the results derived by applying this equation to the ten substances under consideration, using the data already given. For comparison we give in the second column the heats of vaporization that we have used in Tables 4 to 14, and which were obtained either from direct observation or were calculated thermodynamically. In the third column under the heading "Mills" we give the heat of vaporization as calculated from Equation 1, after throwing it into the form:

8. $$L - \mu'(\sqrt[3]{d} - \sqrt[3]{D}) + E_1.$$

The values used for μ' are given below. These values were obtained by averaging what we deemed to be the most accurate values for μ' already given in Tables 4 to 14.

Methyl formate,	121.5	Carbon disulphide,	82.41
Ethyl formate,	107.2	Ammonia,	381.9
Methyl acetate,	109.5	Carbon dioxide,	95.16
Chloroform,	57.97	Nitrous oxide,	88.28
Acetone,	150.8	Sulphur dioxide,	85.80

TABLE 15
Methyl Formate

Temperature	Heat of vaporization			PV/1000
	Ther.	Mills	Crompton	
0°C.	122.23	120.03	131.85	284
40	114.31	111.76	118.22	327
60	106.05	106.27	110.86	331
80	98.50	100.30	103.48	333
100	92.98	94.12	96.33	338
120	86.29	87.10	88.57	337
140	77.97	78.95	79.83	328
160	68.36	69.48	69.91	312
180	56.48	57.90	58.00	288
200	38.80	41.21	41.08	242
210	22.98	25.69	25.50	194
213.5	10.34	12.11	11.99	—

TABLE 16
Ethyl Formate

Temperature	Heat of vaporization		
	Ther.	Mills	Crompton
0°C.	106.83	105.34	117.38
60	96.25	94.93	99.34
80	91.46	90.56	93.48
100	85.83	85.65	87.42
120	80.32	80.33	81.27
140	74.47	74.43	74.75
160	67.21	67.58	67.46
180	59.44	59.81	59.40
200	49.28	50.12	49.54
220	34.47	36.19	35.58
230	22.79	24.72	24.22
233	16.68	18.51	18.11
234	13.91	15.57	15.23

TABLE 17

Methyl Acetate

Temperature	Heat of vaporization		
	Ther.	Mills	Crompton
0°C.	109.34	108.24	119.81
60	98.71	97.67	101.12
80	94.07	93.27	95.15
100	88.48	88.30	88.98
120	82.46	82.73	82.54
140	76.73	76.68	75.88
160	69.96	69.76	68.58
180	61.00	61.35	59.89
200	50.56	51.09	49.58
220	34.87	36.16	34.82
230	20.99	22.62	21.68
232	15.85	17.37	16.63
233	11.70	13.05	12.46

TABLE 18

Chloroform

Temperature	Heat of vaporization		
	Ther.	Mills	Crompton
0° C	67.00	66.94	74.53
20	65.08	65.25	70.90
40	63.13	63.28	67.45
60	61.13	61.08	64.09
100	57.01	56.14	57.61

TABLE 19

Acetone

Temperature	Heat of vaporization		
	Ther.	Mills	Crompton
0° C	140.50	140.45	152.58
20	137.33	137.42	145.36
40	133.44	133.36	138.38
60	128.82	128.47	131.27
100	117.37	117.01	116.70

TABLE 20
Carbon Disulphide

Temperature	Heat of vaporization		
	Ther.	Mills	Crompton
0° C	90.00	90.18	110.23
20	88.02	87.93	105.97
40	85.64	85.36	101.73
60	82.87	82.47	97.46
80	79.70	79.35	93.12
100	76.14	75.97	88.70
120	72.18	72.32	84.15
140	67.83	68.39	79.46
150	65.50	66.35	77.03

TABLE 21
Ammonia

Temperature	Heat of vaporization		
	Observed	Mills	Crompton
—30° C	324.0	324.4	368.8
—20	316.0	316.8	356.4
0	300.0	301.6	333.2
20	284.0	283.8	310.5
40	268.0	266.0	288.4

TABLE 22
Carbon Dioxide

Temperature	Heat of vaporization		
	Observed	Mills	Crompton
—30°C.	75.2	75.60	75.21
—20	69.0	68.30	67.41
0	56.2	56.09	54.97
20	35.0	36.55	35.42
25	26.0	28.43	27.60
30	11.0	15.86	15.39

TABLE 23
Nitrous Oxide

Temperature	Heat of vaporization		
	Observed	Mills	Crompton
−25°C.	66.90	70.62	72.40
−20	65.04	68.76	70.76
0	58 2	56.88	59.27
20	40.0	41.31	43.29
30	22.5	29.67	31.15

TABLE 24
Sulphur Dioxide

Temperature	Heat of vaporization		
	Ther.	Mills	Crompton
−10°C.	94.70	93.15	101.17
0	91.76	90.81	97.65
20	83.80	85.33	90.14
40	79.04	80.01	83.38
60	71.65	73.76	75.99
80	69.89	68.29	70.03
100	61.61	60.54	61.71
120	51.26	50.32	51.05
140	37.69	35.70	35.94
150	25.15	23.19	23.16
155	12.85	11.65	11.59

As shown in these tables the values of the heat of vaporization as given by Crompton's theory are, at low vapor-pressures, uniformly and usually very considerably too high. But at higher temperatures and as the critical temperature is approached the agreement given by Crompton's equation is excellent. And we would call attention to the fact that at the highest temperature for which observation was possible, Crompton's equation gives results more nearly in accord with the values given by Equation 8 than with the thermodynamical or observed results, in the case of methyl formate, ethyl formate, methyl acetate, carbon dioxide, nitrous oxide, and sulphur dioxide. These six substances are the only ones in which the observations are extended to the neighborhood of the critical temperature where Crompton's equation becomes accurate. The significance of a similar agreement we have already discussed (third paper, p. 601, etc.), and here we only point out this continued confirmation of those ideas.

Some Relations at the Critical Temperature

In the third paper, p. 626, we deduced, by an extension of the principles underlying the theory of molecular attraction we have outlined, the equation:

$$9. \qquad L = \mu'(\sqrt[3]{d} - \sqrt[3]{D}) + 0.0_{3}1833\ P\left(\frac{1}{D} - \frac{1}{d}\right) \text{Cals.},$$

where d is the actual and D the theoretical critical density. Also in that paper by a similar application of Crompton's theory we deduced the result:

$$10. \qquad L = \frac{9.154\ T}{m} \log \frac{d}{D} \text{ Cals.}$$

The two equations should give values in agreement if both theories are correct.

We show the results obtained from Equation 9 in Table 25 under the heading "Mills" and the results obtained from Equation 10 under the heading "Crompton." The difference is shown. The agreement is quite close except for carbon disulphide and nitrous oxide, and the divergence may there be due only to inaccurate measurements.

The critical data used is shown in the same table. For methyl formate, ethyl formate, and methyl acetate, the measurements of Dr. Young are used. For carbon disulphide the critical temperature and pressure are from Dewar and the density is from Battelli. For carbon dioxide the data given by Amagat is used. For nitrous oxide the critical temperature and pressure were taken from a table in Travers' Experimental Study of Gases, and the critical density is the value given by Cailletet and Mathias. For sulphur dioxide the critical temperature and density are from Cailletet and Mathias and the pressure from Sajotschewsky.

We also discussed in the third paper an equation (25) holding true for all substances at the critical temperature, that takes the form:

$$11. \qquad \frac{m\mu' \sqrt[3]{d}}{T} = \text{constant.}$$

The mean value of this constant as deduced in that paper for the non-associated substances was 10.76. The values for the constant for the substances now under consideration are given in Table 25 under the heading "Ratio $\frac{\mu}{c}$ to $\frac{\mu}{c'}$." It will be seen that the agreement with the mean value previously given is excellent, except for carbon disulphide and nitrous oxide, a divergence which we believe again points to inaccurate critical data for these substances.

In the fourth paper, p. 415, we showed that it followed from the theories discussed that

$$12. \qquad \frac{PVm}{T} = \text{constant,}$$

where P, V, and T are the critical volume, pressure and temperature. The average value for the substances there examined was 16293. The values for the seven substances now considered are shown in the last column of Table 25. They diverge from the mean value given above more than can be attributed to errors in the data used. We would point out, however, that the three esters (for which the data is most accu-

TABLE 25

	Molecular weight	μ'	Critical			Theoretical density	E_1	$\phi_d - \phi_D$	λ	Latent
			Temperature	Pressure	Density					Mills
Methyl formate, . . .	60.032	121.5	214.0°	45030	0.3489	0.08891	12.01	0.2577	31.31	43.32
Ethyl formate, ...	74.05	107.2	235.3	35590	0.3232	0.08302	10.14	0.2500	26.80	36.94
Methyl acetate, . . .	74.05	109.5	233.7	35180	0.3252	0.08230	10.16	0.2527	27.66	37.82
Carbon disulphide, . .	76.14	82.41	277.7	59356	0.377	0.1314	9.37	0.2140	17.64	27.01
Carbon dioxide, . . .	44.00	95.16	31.35	55404	0.464	0.1283	9.94	0.2698	25.67	35.61
Nitrous oxide, ...	44.08	88.28	39.0	59280	0.41	0.1341	9.47	0.2310	20.39	29.86
Sulphur dioxide, . . .	64.07	85.80	156.0	59964	0.520	0.1434	9.64	0.2807	24.08	33.72

TABLE 25—(*Continued*)

	Heat	Δ	μ/c	μ/c'	Ratio μ/c to μ/c'	$\frac{PVm}{T}$
	Crompton					
Methyl formate, ...	44.08	0.76	475.7	45.11	10.55	15910
Ethyl formate, ...	37.09	0.15	450.1	41.99	10.72	16040
Methyl acetate, ...	37.38	—0.44	459.8	41.78	11.00	15800
Carbon disulphide, ...	30.30	3.29	349.3	42.43	8.23	21770
Carbon dioxide, ...	35.34	—0.27	336.0	31.55	10.65	17260
Nitrous oxide, ...	31.44	1.58	311.9	33.65	9.27	20430
Sulphur dioxide, ...	34.29	0.57	343.3	33.32	10.30	17210

rate) give the best agreement with the mean values, and carbon disulphide and nitrous oxide, as with the preceeding equations, show the largest disagreement.

We would express our thanks to Dr. Young for the data in reference to Biot's formula which he so kindly sent, and to Mr. W. McKim Marriott, Research Assistant in Cornell University Medical College, for a large amount of valuble aid given in checking many of the calculations used in this paper.

Summary

1. In this paper, as in previous papers of this series, our endeavor has been to show that the attraction between the molecules of a liquid varies inversely as the square of the distance apart, and that consequently the law of gravitation holds between the molecules of a liquid. An equation,

$$\left(\frac{L - E_1}{\sqrt[4]{d} - \sqrt[4]{D}} = \text{constant}\right),$$

was deduced, embodying this idea, and we wish to summarize the results obtained in testing this equation.

Thirty-one substances have been examined, the examination extending over a wide range of temperature. Of these substances the measurements available for three of them, *viz.*, stannic chloride, nitrous oxide, and sulphur dioxide, are known to be less accurate than the measurements for the others and we wish to place them in a class by themselves. Five of the substances, *viz.*, water, three alcohols, and acetic acid, are known to have molecular association and these substances we also place in a class to themselves, for there is no reason, *a priori*, to suppose the unmodified equation applicable to them. The remaining twenty-three substances include ethyl ether; acetone; four straight-chained paraffins, *viz.*, normal pentane, normal hexane, normal heptane, and normal octane; one paraffin with a singly branched chain, iso-pentane; two paraffins with a doubly branched chain, *viz.*, di-isopropyl and di-isobutyl; benzene; hexamethylene; four mono-halogen derivatives of benzene, *viz.*, fluo-benzene, chlor-benzene, brom-benzene, and iodo-benzene; chloroform; carbon tetrachloride; three esters, *viz.*, methyl

formate, ethyl formate, and methyl acetate; carbon disulphide; carbon dioxide; and ammonia. Probably acetone and ammonia are liquids whose molecules are associated. These twenty-three substances are, therefore, representative of very large and varied classes of chemical compounds. In two tables (second paper, Table 1; this paper, Table 3), we record for these twenty-three substances the results of the tests of the equation, $\frac{L - E_1}{\sqrt[3]{d} - \sqrt[3]{D}} = \text{constant}$. (All of the tests possible were made, and all of the tests made were recorded in the two tables above mentioned, except those at sub-intervals of 10° C.)

Excepting the divergent tests within ten degrees of the critical temperature it was found that of the 378 tests remaining, 349 were within two percent of the mean values of the constant adopted, and only 29 showed a divergence from the constant greater than two percent. Of these divergent values only 3 were greater than five percent, *viz.*, iodo-benzene at 190°; methyl formate at 200°; ethyl formate at 220°.

Since the errors of observation are compounded and often largely multiplied in their relative effect upon the constant, there can be no question but that the two percent margin allowed for the effect of errors of observation is an exceedingly reasonable limit. The 29 tests that showed a divergence from the mean constant greater than two percent were shown to occur at places where there was for some reason stated a decreased accuracy in the measurements and the measurements used were shown to give slightly irregular curves when examined, or it was shown that the errors of observation were greatly multiplied in the calculations. In detail these divergences were explained as follows:

(*a*) Due to the defects pointed out in Biot's formula for vapor-pressure: Ether at 190°; normal octane at 0°; chlor-benzene at 240°, 250°, 260°, 270°; brom-benzene at 30°; methyl formate at 180°, 190°, 200°; ethyl formate at 210°, 220°; methyl acetate at 220°. Also all divergences within ten degrees of the critical temperature.

(*b*) Due to direct multiplication of error of observation: carbon dioxide at 20°.

(*c*) Occurring at the point where the volume of the vapor could be least accurately measured, and accompanied by an irregularity in the PV curve when plotted against the temperature: Di-isopropyl at 120° to 190° inclusive; brom-benzene at 160°, 170°; iodo-benzene at 190°; 200°, 210°; methyl formate at 30°, and 40°.

It was shown that the error attributed to Biot's formula could usually be corrected quantitatively and that after correction the agreement was satisfactory up to and at the critical temperature itself, except for di-isopropyl, normal heptane, normal octane, and methyl formate. This remaining divergence constitutes the sole unexplained disagreement of the 397 tests shown on these twenty-three substances.

Concerning the substances stannic chloride, nitrous oxide, and sulphur dioxide, it was concluded that their divergence from the mean value of the constant was not more pronounced than the probable inaccuracy of the data used made possible.

We believe, therefore, that the evidence has established the truth of the equation, $\frac{L - E_1}{\sqrt[3]{d} - \sqrt[3]{D}} = \text{constant}$, beyond a reasonable doubt. We would not say that it is equally certain that this equation can have no other basis than the law of attraction assumed, but the equation was deduced from the assumed law of attraction as a basis and such a conclusion appears, therefore, at the present time the most reasonable.

If the assumed law of attraction is true other results should likewise follow and these results we expect to discuss in several papers bearing upon the relation between the specific heat of solid, liquid and gas, upon the total energy of a molecule, in so far as it is subject to measurement, and upon the energy relations at the boiling-point.

2. In this paper an equation given by Crompton, $L = 2RT \log_\epsilon \frac{d}{D}$, was further examined and the conclusion hitherto reached was confirmed, *viz.*: This relation gives results for the

heat of vaporization uniformly too high at low vapor-pressures, but at high vapor-pressures, in the neighborhood of the critical temperature, the equation is accurate.

3. Some relations at the critical temperature, already pointed out, are examined further and are for the most part confirmed.

University of North Carolina,
July 24, 1905.

ELECTRODEPOSITION OF COPPER UPON IRON

BY OLIVER W. BROWN AND FRANK C. MATHERS

Most common metals as iron or zinc will precipitate copper when simply immersed in an acid copper-plating solution. This always results in a non-adherent deposit of copper of no value to the plater. Under the same conditions, iron and zinc have no effect upon an alkaline cyanide bath. The acid-plating solutions are always used where the cathode materials as copper, lead, carbon, etc., make it possible, because of their very high efficiencies and the high current densities at which they will work. But with iron or zinc cathodes, alkaline copper baths must be used. All of the alkaline copper-plating solutions recommended by Pfanhauser in "Elektroplattirung," page 332, contain cyanide. Cyanide is objectionable, both on account of its very poisonous properties and its high cost. In the case of cyanide copper-plating solutions, the anode soon becomes covered with a slimy green precipitate, which causes bad local action, interferes with the proper working of the bath, and may reduce the efficiency of anode corrosion. This green precipitate causes very unequal corrosion over the surface of the anodes, resulting in deep pitting. The bath voltage is also greatly increased. The formation of the precipitate over the surface of the anode can be prevented only by the addition of large amounts of cyanide. Pfanhauser states that the current efficiency of his cyanide copper-plating bath is 80 percent. This probably refers to the cathode, as no mention is made of anode corrosion. When the bath becomes old the efficiency drops considerably below 80 percent.

In our experiments the plating solution was placed in a glass battery jar, 12 cm. long, 15 cm. high, and 6 cm. wide. The volume of the plating solution was generally about 700 cc. A copper voltameter was always placed in series with the plating bath. The electrodes of the bath were connected to a switchboard, normal calomel electrode and standard cells, arranged for measuring the discharge potentials of the cathode, of the anode,

and also the total polarization electromotive force of the bath. In the calculations, the value of the calomel electrode was taken as —0.56 volt. Unless otherwise stated, the electrodes were 100 sq. cm. area on one side. Iron cathodes were tried in each bath in order to observe the quality of the copper deposited upon iron, but copper cathodes were used in making measurements for the tables and for quantitative experiments. The electrodes were placed 5 cm. apart, unless otherwise stated, and the solution was not stirred during electrolysis.

The beautiful and firm deposit obtained in the ammonia method for the quantitative determination of copper, suggested that a similar solution might make a good plating bath for the deposition of copper upon iron. A bath of the following composition was tried:

100 grams copper sulphate,
120 cc ammonium hydrate,
1000 cc water.

This bath attacked iron cathodes, and the anode was always covered with a basic copper slime during electrolysis, which made quantitative work impossible. Experiments were also made with an ammonia-bath containing

60 grams copper sulphate,
66 cc ammonium hydrate,
1000 cc water

This bath gave equally poor results even with as low a current density as 0.2 ampere per square decimeter. However, both of these solutions gave excellent deposits of copper upon copper cathodes. The addition of more ammonia and ammonium salts did not improve the working of the baths.

The "Weil" bath, described in Langbeins's "Electrodeposition of Metals," page 229, was next tried. This bath contains

159 grams sodium potassium tartrate,
31.5 " copper sulphate,
50.4 " caustic soda,
1000 cc water.

This gives good anode corrosion and fine cathode deposits as long as the current density is not above 0.25 ampere per square decimeter. The deposit upon an iron cathode was as firm, smooth and bright as upon copper. The experimental data with this bath are as follows:

Amp.	Bath tension Volt	Discharge potential		Total polarization E. M. F. of cell Volt	Current efficiency	
		at Cathode Volt	at Anode Volt		at Cathode Percent	at Anode Percent
0.25	0.6	0.36	—0.104	0.48	95.2	101.7
0.4	0.8	0.207	—0.192	0.75	—	101.7

In the second experiment the cathode deposit was so spongy that it could not be accurately weighed. To get a bath that would work at a higher current density and also give a better cathode efficiency, the following was next tried:

159 grams sodium potassium tartrate,
61 " copper sulphate,
50 " sodium hydroxide,
50 " sodium chloride,
1000 cc. water.

With a cathode area of 50 sq. cm. the following results were obtained:

Amp.	Bath tension Volt	Discharge potential		Total polarization E. M. F. of cell Volt	Current efficiency	
		at Cathde Volt	at Anode Volt		at Cathode Percent	at Anode Percent
0.306	0.73	0.306	—0.177	0.427	100.88	100.7
0.31	0.75	0.31	—0.161	0.456	101.1	102.2
0.36	0.7	0.36	—0.132	0.39	100.28	100.76
0.32	0.69	0.32	—0.173	0.27	99.48	—
0.32	0.85	0.32	—0.132	0.545	100.6	100.7

In the above experiments the deposited copper was very bright, dense and coherent, and was just as good when deposited upon iron as upon copper. As the cathode used had an area of 50 sq. cm.,

the current density per square decimeter is equal to twice the current strength. The probable cause of the current efficiencies going above 100 percent is the presence of some cuprous salts in the bath. As the bath resembles Fehling's solution, it is easy to see how it might be reduced perhaps by the current itself in any experiment in which the efficiency was below 100 percent or by the introduction of some organic impurity.

When the above bath was diluted with an equal volume of water, the following results were obtained:

Amp.	Bath tension Volts	Discharge potential		Total polarization E. M. F. of cell Volt	Current efficiency	
		at Cathode Volt	at Anode Volt		at Cathode Percent	at Anode Percent
0.225	0.8	0.204	—0.174	0.366	100.91	100.95
0.35	1.71	0.635	—0.75	1.44	100.81	15.5
0.34	1.6	0.516	—0.693	1.19	101.68	34.1

In the third experiment, 50 grams of salt were added to each 1000 cc. of solution. In the first of these experiments, the precipitate was bright and firm, but in the last two the cathode deposit was black and spongy.

Under certain conditions the anode assumes the passive state and then it does not dissolve but merely becomes covered with a thin coating, probably of cuprous oxide. This is clearly shown in the following experiments, which also illustrate the ease and accuracy by which one can tell what is happening in the bath from the discharge potential readings.

	Amp.	Volts	Cat. disc. Volt	An disc. Volt	T. polar. Volts	Effic. cath. Percent	Effic. anode Percent
At start	0.55	—	0.312	—0.162	0.481	—	—
At end	0.54	1.6	0.148	—0.786	0.716	100.52	39.50
At start	0.42	1.5	0.22	—0.81	1.017	—	—
At end	0.42	—	0.163	—0.796	0.978	101.02	0.12

After cleaning the anode in nitric acid and washing in water, the discharge potential reading was —0.132 volt. At the be-

ginning of the first experiment the anode was dissolving quantitatively as shown by the discharge reading, but the high discharge potential at the end of the experiment indicates that the corrosion had ceased. The very low anode efficiency of 39.5 percent proves this. The same anode, without any cleaning, was used in the second experiment in the above table, at a current density at which it should have dissolved, but the anode discharge potential, both at the start and at the end, indicates that it was not dissolving and the anode current efficiency of only 0.12 percent proves this fact. After cleaning the anode in nitric acid, the discharge reading of —0.132 volt shows that the passive state of the electrode is removed by the acid treatment.

In using the tartrate-plating solutions, it was noticed that after a certain lapse of time, they failed to give as good results as when new, that is, the anode efficiency was not as good at the higher current densities. The cathode deposit was as bright and firm as ever. It was first thought that the tartrate was being used up. However, the addition of more of this salt did not improve the anode corrosion. It was next thought that the carbon dioxide of the air was gradually changing the caustic soda of the bath to sodium carbonate, thus injuring the plating solution. To test this, a vigorous current of carbon dioxide gas was passed for ten minutes through a bath, which was in perfect working order. This solution then gave a black, spongy cathode deposit and the anode was covered with a green, slimy precipitate and was deeply pitted. It was impossible to accurately weigh the electrodes. No way of precipitating out the carbon dioxide by the addition of such reagents as milk of lime or barium hydrate was found as these substances precipitate calcium or barium tartrate. Later experiments show that the addition of as much as 15 grams of caustic soda per liter will completely restore one of these baths. As an example, the following data is from a bath, which was working badly, to which was added 15 grams of caustic soda per liter. The cathode surface was 50 sq. cm. With a current of 0.2 ampere and a voltage of 0.9, the cathode discharge potential was 0.266 volt, the anode discharge potential was —0.133 and the total polarization

electromotive force was 0.459. The cathode efficiency was 100.12 percent and the anode efficiency was 102.42 percent. The cathode deposit was bright and firm.

In order to get a plating solution which would not change composition on contact with air, several baths were made containing sodium carbonate instead of caustic soda. In all of these the cathode deposit was smooth and adherent, but the anode did not dissolve. Salt, sodium carbonate, potassium chlorate, and tartrates were added, temperatures from 30 to 85° C, and high and low current densities were tried but in no case did the anode appreciably corrode.

A bath of the following composition has given good results, when plating copper upon iron :

159 grams sodium potassium tartrate,
60 " copper sulphate.
50 " caustic soda,
50 " sodium chloride,
1000 cc water.

After 136 hours electrolysis with 0.2 ampere and a cathode of 50 sq. cm. surface and an anode of 100 sq. cm., the bath was still giving excellent results. Then after this 136 hours' electrolysis, a current of 0.3 ampere per square decimeter gave an anode discharge of —0.074 volt which immediately changed to —0.88 volt, showing that at this place the anode ceased to corrode. The addition of 15 grams of caustic soda per liter brought the anode discharge to —0.133 volt with a current density as high as 0.47 ampere per square decimeter. This very clearly shows that the addition of caustic soda prevents the formation of slime and restores a high efficiency in anode corrosion.

Experiments were next tried to determine the effect of sodium chloride, sodium potassium tartrate, copper sulfate, and sodium hydroxide upon the copper deposit and also upon the efficiency of anode corrosion. In all of these experiments, one cathode and two anodes of copper, 10 by 10 cm. were used. The two anodes were placed 5 cm. apart and the cathode was hung between them. This gave an active surface of 2 sq. dcm. for

both the cathode and the anode. All readings were taken after 20 minutes' electrolysis.

TABLE I

Effect of varying amounts of sodium chloride. The plating solution contained, copper sulphate 60 grams, sodium hydroxide 50 grams, sodium potassium tartrate 159 grams, water 1000 cc, and varying amounts of sodium chloride.

Grams NACl per liter	Bath tension Volt	Amperes per square decimeter at anode and cathode	Discharge potential		Total polarization E. M. F. of cell	Nature of cathode deposit
			at cathode Volt	at anode Volt		
0	0.0	0.0	—0.154	—0.154	0.0	
0	0.38	0.1	—0.212	—0.291	0.229	Bright
0	—	0.35	—0.067	—0.216	—	"
0	0.82	0.4	+0.392	—0.094	0.490	"
0	0.90	0.5	+0.322	—0.098	0.490	Bright
0	1.00	0.6	+0.378	—0.098	0.571	Burned
0	1.30	0.9	+0.490	—0.126	0.761	"
0	1.20	1.04	+0.518	—0.112	0.854	"
0	1.92	1.07	+0.548	—0.686	1.501	"
50	0.43	0.1	±0.0	—0.168	0.241	Bright
50	0.8	0.25	+0.28	—0.140	0.456	"
50	0.89	0.3	+0.296	—0.112	0.414	"
50	1.00	0.4	+0.468	—0.132	0.691	Burned
50	1.2	0.75	+0.845	—0.14	0.913	"
50	1.9	1.0	+0.711	—0.798	1.627	"
100	0.55	0.1	+0.098	—0.134	0.347	Dark
100	1.00	0.3	+0.274	—0.102	—	"
100	1.16	0.4	+0.658	—0.148	0.851	"
100	1.28	0.5	+0.577	—0.151	0.831	"
100	2.11	0.6	+0.784	—0.882	1.753	"

Results in the above table show that with no salt in the plating bath, a current density of 0.1 to 0.5 ampere per square decimeter gave a bright, dense and adherent deposit, which was as good upon iron as upon copper. With 50 grams of salt per liter, good cathode deposits were gotten with currents of 0.1 to 0.3 ampere per square decimeter, while with 100 grams of salt per liter, the cathode deposits obtained at all densities were dark. The anode discharge potentials show that the maximum current density per square decimeter, which will give theoretical

efficiency in anode corrosion, is 1.04 amperes with no salt, 0.75 ampere with 50 grams of salt, and 0.5 ampere with 100 grams of salt per liter. Hence the addition of sodium chloride is harmful to the cathode deposit and decreases the efficiency of anode corrosion, in all cases.

TABLE 2

Effect of varying amounts of copper sulfate. The plating solution contained sodium hydroxide 60 grams, sodium potassium tartrate 159 grams, water 1000 cc, and varying amounts of copper sulfate.

Grams of $CuSO_4 5H_2O$ per 1000 cc.	Bath tension Volts	Amperes per square decimeter at anode and cathode	Discharge potential		Total polarization E. M. F. of cell	Nature of cathode deposit
			at cathode	at anode		
40	0.4	0.1	—0.012	—0.147	0.174	Bright
40	0.98	0.3	+0.269	—0.139	0.47	"
40	1.00	0.4	+0.466	—0.139	0.655	Slightly burned
40	1.35	0.5	+0.466	—0.139	0.63	Burned
40	1.12	0.6	+0.494	—0.144	0.619	"
40	2.2	0.7	+0.409	—0.610	1.125	"
60	0.38	0.1	+0.212	—0.291	0.229	Bright
60	0.9	0.5	+0.322	—0.098	0.49	"
60	1.	0.6	+0.378	—0.098	0.571	Burned
60	1.2	1.04	+0.518	—0.112	0.854	"
60	1.92	1.07	+0.548	—0.684	1.501	"
80	0.4	0.1	+0.03	—0.15	0.202	Purple deposit
80	0.65	0.2	+0.181	—0.147	0.36	Dark
80	0.82	0.3	+0.269	—0.145	0.404	Bright
80	0.95	0.4	+0.269	—0.161	0.410	"
80	1.00	0.5	+0.232	—0.150	0.379	"
80	1.9	0.6	+0.246	—0.799	1.298	Burned

The results in the above table show that with 40 grams of copper sulfate per liter in the plating bath, a current density per square decimeter of from 0.1 to 0.3 amp. gives good cathode deposits; with 60 grams, 0.1 to 0.5 amp. may be used, while with 80 grams a density of from 0.3 to 0.5 gives good deposits. When using 80 grams of copper sulfate per liter, a current density below 0.3 ampere per square decimeter gave a deposit which had a purple, velvety appearance. The maximum current density

at the anode which would give theoretical anode corrosion was 0.6 ampere for 40 grams, 1.04 for 60 grams, and 0.5 for 80 grams of copper sulfate per liter. The best results at both the anode and the cathode were gotten when 60 grams of copper sulfate per liter were used.

TABLE 3

Effect of varying amounts of sodium potassium tartrate. The plating solution contained copper sulphate 60 grams, sodium hydroxide 50 grams, water 1000 cc, and varying amounts of sodium potassium tartrate.

Grams of Rochelle salt per 1000 cc.	Bath tension volts	Amperes per square decimeter at anode and cathode	Discharge potential		Total polarization E. M. F. of cell	Nature of cathode deposit
			at cathode Volt	at anode Volt		
100	0.52	0.1	+0.126	—0.194	0.353	Slightly dark
100	0.65	0.2	+0.238	—0.182	0.498	" "
100	0.90	0.3	+0.294	—0.194	0.574	Bright
100	0.80	0.4	+0.238	—0.157	0.577	"
100	1.80	0.5	+0.294	—0.826	1.349	"
100	2.15	0.6	+0.280	—0.854	1.326	Slightly dark
159	0.38	0.1	+0.212	—0.291	0.229	Bright
159	0.9	0.5	+0.322	—0.098	0.490	"
159	1.0	0.6	+0.378	—0.098	0.571	Burned
159	1.2	1.04	+0.518	—0.112	0.854	"
159	1.92	1.07	+0.548	—0.684	1.501	"
209	0.68	0.1	+0.207	—0.125	0.466	Bright
209	0.80	0.2	+0.297	—0.056	0.522	"
209	0.90	0.3	+0.283	—0.056	0.449	"
209	0.80	0.35	—	—	—	Burned
209	1.29	0.4	+0.325	—0.153	0.632	"
209	1.45	0.7	+0.301	—0.153	0.660	"
209	2.10	0.8	+0.446	—0.743	1.169	"

These results show that the limits for the current densities which will give good cathode deposits are 0.3 and 0.5 ampere with 100 grams, 0.1 and 0.5 with 159 grams, and 0.1 and 0.3 with 209 grams of sodium potassium tartrate per liter. The maximum density, which gives theoretical anode corrosion is 0.4 ampere with 100 grams, 1.04 amperes with 159 grams, and 0.7 with 209 grams of sodium potassium tartrate per liter.

TABLE 4

Effect of varying amounts of sodium hydroxide. The plating solution contained copper sulphate 60 grams, sodium potassium tartrate 159 grams, water 1000 cc, and varying amounts of hydroxide.

Grams caustic soda per 1000 cc.	Bath tension Volts	Amperes per square decimeter at anode and cathode	Discharge potential		Total polarization E. M. F. of cell	Nature of cathode deposit
			at cathode Volt	at anode Volt		
25	0.7	0.1	+0.258	−0.181	0.525	Bright
25	1.6	0.2	+0.213	−0.883	1.112	"
25	1.7	0.3	—	—	—	"
25	2.0	0.4	+0.213	−0.715	0.936	Dark
Cleaning electrodes in acid gave no better anode corrosion.						
35	0.4	0.1	−0.026	−0.158	0.177	Black
35	0.7	0.2	+0.184	−0.181	0.129	Dark
35	0.92	0.3	+0.243	−0.184	0.494	"
35	1.60	0.35	—	—	—	Slightly dark
35	1.80	0.4	+0.297	−0.799	1.256	Bright
35	2.12	0.5	+0.494	−0.855	1.322	Dark
40[1]	0.28	0.05	−0.240	−0.407	0.177	Purple
40	0.5	0.175	−0.130	−0.366	0.341	Bright
40	0.9	0.450	+0.084	−0.028	0.473	"
40	0.95	0.50	+0.084	−0.014	0.526	Dark
40	1.00	0.55	+0.084	−0.519	1.23	"
40	2.00	0.6	+0.052	−0.615	1.372	"
45	0.4	0.1	+0.126	−0.35	0.294	"
45	0.7	0.2	−0.028	−0.168	0.35	Bright
45	0.9	0.5	+0.084	−0.098	0.462	"
45	1.3	0.6	+0.336	−0.084	0.644	Dark
45	1.1	0.8	+0.112	−0.028	0.665	"
45	1.8	0.9	+0.089	−0.616	1.23	"
50	0.38	0.1	+0.212	−0.291	0.229	Bright
50	0.9	0.5	+0.322	−0.098	0.49	"
50	1.0	0.6	+0.378	−0.098	0.571	Burned
50	1.2	1.04	+0.518	−0.112	0.854	"
50	1.92	1.07	+0.548	−0.684	1.501	"
55	0.3	0.1	−0.238	−0.387	0.174	Dark
55	0.6	0.2	−0.112	−0.244	0.316	Bright
55	0.9	0.5	+0.084	−0.126	0.453	Slightly spongy
55	1.1	0.6	+0.224	−0.112	0.588	Dark
55	1.4	1.0	+0.154	−0.196	0.728	"
55	2.0	1.1	+0.154	−0.896	1.36	"

[1] Mr. Henry B. Wilson, Jr. did the experimental work upon the solutions containing 40, 45, and 55 grams of sodium hydroxide per liter.

TABLE 4—(*Continued*)

Effect of varying amounts of sodium hydroxide. The plating solution contained copper sulphate 60 grams, sodium potassium tartrate 159 grams, water 1000 cc, and varying amounts of hydroxide.

Grams caustic soda per 1000 cc.	Bath tension Volts	Amperes per square decimeter at anode and cathode	Discharge potential		Total polarization E. M. F. of cell	Nature of cathode deposit
			at cathode Volt	at anode Volt		
60	0.4	0.1	—0.093	—0.196	0.207	Dark
60	0.7	0.2	+0.098	—0.129	0.378	Bright
60	0.82	0.4	+0.252	—0.126	0.52	"
60	1.00	0.5	+0.235	—0.126	0.574	Slightly spongy
60	1.1	0.6	+0.238	—0.080	0.761	Dark
60	1.45	0.9	+0.426	—0.179	0.621	"
60	2.00	1.0	+0.462	—0.658	—	"
70	0.35	0.1	—0.037	—0.237	0.271	"
70	0.80	0.2	+0.185	—0.125	0.428	Slightly spongy
70	0.8	0.3	+0.244	—0.195	0.509	Slightly spongy
70	1.2	0.4	+0.269	—0.096	0.705	Dark
70	1.2	0.9	+0.494	—0.195	0.826	"
70	2.16	1.0	+0.494	—0.771	1.408	"

	Grams NaOH per 1000 cc.	Bath tension Volt	Amperes per square decimeter at anode and cathode	Discharge potential		Total polarization E. M. F. of cell	Nature of cathode deposit	Current efficiency at	
				at cathode Volt	at anode Volt			Cathode Percent	Anode Percent
	40	0.45	0.17	—0.162	—0.308	0.322	Spongy	—	103.7
	45	1.00	0.5	+0.56	—0.112	0.462	Dark	—	101.57
At beginning, . . .	45	0.9	0.4	±0.0	—0.098	0.434	Bright	—	—
At end, ...	45	0.9	0.4	±0.0	—0.126	0.462	"	100.45	101.75

The results of this table are summed up below.

Grams caustic soda per liter	25	35	40	45	50	55	60	70
Limits of current density per square decimeter, giving good deposits	0.1 to 0.3	0.4	0.17 to 0.45	0.1 to 0.5	0.1 to 0.5	0.2 to 0.4	0.2 to 0.4	Dark at all densities
Maximum current density per square decimeter, giving theoretical anode corrosion	0.1	0.3	0.5	0.8	1.04	1.0	0.9	0.9

These results show that a bath with 50 grams of sodium hydroxide per liter admits of the largest range of current densities, which will give theoretical current efficiencies at both the anode and the cathode and also a bright, adherent deposit of copper.

The above tables show that the best bath is as follows:

60 grams copper sulfate,
50 " sodium hydroxide,
159 " sodium potassium tartrate,
1000 cc water.

The best working conditions for the above bath are a current density at the cathode of 0.1 to 0.5 ampere per square decimeter and a maximum density per square decimeter at the anode of not over 1.04 amperes. If at any time a green precipitate should begin to form on the anode, a little caustic soda—three or four grams per liter—should be added. The substitution of potassium hydroxide for sodium hydroxide and the warming of the bath were detrimental to its working. Rolled, electrolytic, and cast copper anodes worked equally well. Under the conditions of the above experiments, the anode ceases to give theoretical corrosion whenever the electrode tension reached a value much above 1.3 volts. In all of our quantitative experiments, the current efficiency for anode corrosion was theoretical if the anode discharge potential had a value of —0.3 or less, but whenever the value changed to —0.6 volt or greater, the anode corrosion became very poor.

The tartrate baths are superior to the cyanide baths, in that they are non-poisonous, do not give off an offensive gas during electrolysis, will work at a higher anode density, give as good cathode deposits, require a lower voltage, and yield a current efficiency of 100 percent at both electrodes.

The bath requires the addition of small amounts of caustic soda from time to time. However, it is not inferior to the cyanide bath in this respect as the latter requires the addition of potassium cyanide.

Electrochemical Laboratory of Indiana University,
September, 1905.

ON CRYSTALLINE HABIT

BY F. G. COTTRELL.

The first attempt to point out and treat the factors which determine what we know as crystal habit (*i. e.*, the relative size and frequency of occurrence of the various faces which are possible on any given crystal) seems to have been made by Gibbs[1] in that remarkable contribution which has served as the starting point for so much of our present physical chemistry.

He there devoloped the fundamental equations for the equilibrium of a crystal in its saturated solution including the terms due to surface tension of the different faces, and points out that for complete equilibrium $\Sigma(\sigma s)$ must have its minimum value; s being the total area of all the faces of a given "form," σ the surface tension for that form in contact with saturated solution, and the summation being extended to include all the possible forms which may appear on the crystal. This is the direct analogue of the principle that a drop of liquid tends to reduce its surface to a minimum and become a sphere. Practically, the same idea was later put forward independently and without knowledge of Gibbs' work by Curie[2] and has found its way thence into the general crystallographic literature, while the more complete theoretical treatment of Gibbs seems to have almost wholly escaped recognition.

According to this view of crystalline habit those faces which are developed by the crystal in greatest extent should have, in contact with the solution, the lowest surface tension. In agreement with this are an interesting set of measurements by Berent[3] on sodium and potassium chlorides though his method as he points out does not furnish a real proof.

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[1] J. W. Gibbs: Trans. Conn. Acad., Vol. 3, 489 et ff. (April, 1878).

[2] P. Curie: Bull. Soc. Min., 8, 145 (1885). Abst. in Zeit. Kryst., 12, 651.

[3] S. Berent: Zeit. Kryst., 26, 529 (1896). See also A. Rota, Rend. Acc. Lincei (5), 7, 125–129 (1898), and Beibl., 23, 237, who worked with alum. A. Pockels, Naturwiss. Rundsch., 14, 383 (1899). and Beibl., 24, 13, has, however, called the results of both authors into question.

That this tendency for the decrease of total surface energy must tend to establish the particular crystal habit predicted by the equations of Gibbs and Curie when a crystal is left quietly in its saturated solution seems incontestable. Beyond this, however, certain questions arise, *viz.*: (1) Through what channels and by what mechanism would the necessary transfer of material be brought about? (2) How long would this take? (3) During the growth of the crystal (a dynamic process) would these conditions (derived from consideration of a system almost in equilibrium) still be the determining factors?

As to question (1), under isothermal conditions the only way open to transfer of material from one face to another seems through an actual difference in solubility on the two faces in question and a steady diffusion which may be aided by artificial convection. That surface-tension can actually change the solubility of a solid to a very appreciable extent has been conclusively shown by the work of Hulett[1] and others on fine powders; but it has been likewise demonstrated that this effect ceases to be appreciable to our methods of measurement long before the bodies reach anything like the dimensions which we usually have to deal with in the crystals whose habit is under discussion.

This point was clearly recognized by Gibbs and discussed by him. Thus referring to the equation (666) of his original text which gives for equilibrium the ratio of the areas of different faces in terms of their surface-tension and angles of intersection, he says, "This condition will not be affected by a change in the size of a crystal while its proportions remain the same. But the tendencies of similar crystals towards the form required by this condition as measured by the inequalities in composition or the temperature of the surrounding fluid which would counterbalance them will be inversely as the linear dimensions of the crystals as appears from the preceding equation."

In order to throw some light on question (2) as regards even fairly small crystals, the following experiment was carried out, some three years ago, in the Physical Chemistry Institute at

[1] G. A. Hulett: Zeit. phys. Chem., 37, 385 (1901).

Leipsic. A glass rod drawn out to a point and bearing at its apex, cemented with wax, a minute fragment of sodium chloride was introduced into a saturated solution of the same salt plus something over 10 percent of urea, the whole was placed in a large thermostat at 25° C. (variation seldom exceeding 0.01° C.) and allowed to undergo spontaneous evaporation until a crystal of some 2 to 3 millimeters across was developed on the end of the rod. Meanwhile, a saturated solution of the same salt without the urea had been prepared, a small test-tube filled with it and a few undissolved crystals added, the whole tightly stoppered and placed upon one of the rotating axes below the surface of the water in the thermostat and left there a couple of days to ensure saturation at that temperature. The rod and crystal were now removed from the urea solution rinsed with a little of the pure saturated sodium chloride solution and the free end of the rod fastened into the rubber stopper of the tube of pure solution, so that the crystal was held at about the center of the tube. A few loose crystals of pure salt and an air bubble were left in the tube which facilitated stirring and the whole, after sealing with wax, was returned to the rotating axis and remained there, making about five revolutions per minute for over two months. When taken from the solution with urea the salt crystal was a perfect octahedron (as is always obtained from such solutions). It was examined the next day (without removal from the tube) and by the aid of a hand lens a barely perceptible truncation of the octahedron corners by cubic faces could be detected. This may have been produced by solution and recrystallization as a whole, due to fluctuation of temperature attendant upon its transfer from one solution to the other, or it may have been due to the causes discussed by Gibbs and Curie. The fact that although the truncation was very slight; still decided differences could be observed between the different corners leads me to favor the former of these explanations, as, if it were due to the second cause, we should expect greater uniformity. During the remainder of the two months and more that the crystal was under observation no further growth of these faces could be detected.

This experiment together with the fact that from pure water solution it is almost impossible to crystallize an octahedron face on a sodium chloride crystal, make it apparent how very slight the difference in solubility on the two faces must be even under the most favorable conditions, such as the above. Hulett[1] has recently reported similar conditions in the case of gypsum.

Finally in regard to question (3): The magnitude of the effect of this difference in solubility at the different faces upon their rate of growth. If a crystal is to grow in solution the concentration of the mass of the latter must be maintained slightly above the saturation point while the layers in contact with the crystal will be kept down nearly or quite to this point. Material is thus transported to the crystal by the process of diffusion and, if other conditions are equal, the rate of its growth will be determined by the rate of the diffusion. For our present qualitative purpose, with crystals of moderate size, we may consider diffusion as essentially linear and normal to each crystal face. Its rate will then be proportional to the degree of supersaturation of the bulk of the solution referred to the particular solid face. If this degree of supersaturation is of the same order of magnitude as the differences between the saturation concentration for solution at the different faces, then this latter difference would undoubtedly be an important factor in determining the rate of deposit and consequently the habit. Were this the case, however, the rate of growth of a crystal would be of the same order of magnitude as the rate of change from one face to the other in the experiment on sodium chloride cited above, for the processes would be strictly analogous.

The more rapidly the crystals are grown, *i. e.*, the greater the degree of supersaturation of the solution, the less pronounced would be the difference in the diffusion to the different faces and the more nearly would all possible faces develop to the same extent. From this standpoint, a moment's consideration of the exceedingly slow rate of transformation indicated by the above experiment, will I think convince one that at the rate we

[1] G. A. Hulett: Jour. Am. Chem. Soc., 27, 53 (1905).

ordinarily crystallize substances in the laboratory, even when we are seeking typically developed crystals, for measurement, this factor can have little or no practical significance.

This forces upon us the conclusion that the practical explanation for crystal habit must not be sought for in any of the terms of the equations simply defining conditions of *equilibrium* of the crystal and its saturated solution, but on the contrary must be sought in terms defining the *rate of growth* of the various faces which disappear entirely in the final equations of equilibrium. Workers in this field have been far too hasty in applying the equations of statics to dynamic measurements. A paper by Schenck[1] on dynamics of crystals is a good example of this.

It was in the hope of being able to analyze these velocity terms and reach some at least of them by independent experiment that the foregoing has been withheld until now; but although considerable time and effort has been expended, no satisfactory method of attack has been found. We may, of course, consider the processes at the surface of and in the solid phase (*i. e.*, arrangement of crystal elements) as distinct from those in the liquid phase (supply of material by diffusion if from a solution or dissipation of heat if from fusion). The fact that crystals separated by cooling of a pure melt show a distinct habit, points strongly to the first type as a responsible factor, while the change of habit on addition of a substance to the solution as in the above experiments makes it probable that the second type of process must also be included in any general explanation of crystal habit. In conclusion, it should be noted that the forces underlying processes of the first type have been treated theoretically from one standpoint at least by Sohncke[2] and the recent work of Nernst and Brunner[3] on reaction velocity in heterogenous systems has emphasized the utility of clearly separating these two types of process.

[1] R. Schenck: Centrbl. Miner., 1, 313–318 (1900).
[2] L. Sohncke: Zeit. Kryst., 13, 220 (1888).
[3] Nernst and Brunner: Zeit. phys. Chem., 47, 52–103 (1904).

To sum up in the above note it has been pointed out: (1) That what is commonly known in crystallographic and mineralogical literature as Curie's theory of crystal habit was put forward in a more exact and complete form by J. W. Gibbs seven years before the paper by Curie. (2) That the true explanation of crystal habit from the practical standpoint must be sought in terms representing velocities and not equilibrium, fresh experimental evidence for this conclusion being presented.

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NEW BOOKS

Les Origines de la Statique. *By P. Duhem. Tome premier. 16 × 25 cm; pp. iv + 360. Paris: A. Hermann, 1905. Price: paper, 10 francs.*—Duhem's grasp of mathematical physics, his fluency and powers of exposition, are well known. With the resources of his literary scholarship most chemists are less familiar. True, a small book called *L'Évolution de la Mécanique* (Paris, 1903) appeared not long ago, in which dynamics, regarded from the broadest thermodynamic point of view, is treated historically with the ease of complete mastery. But these were subjects with which the name of Duhem has been more or less familiarly associated. For the present departure, however, the reader is quite unprepared; the author goes back to Greek, Latin, and other ancient or medieval texts, and lingers over them with a degree of fondness quite unusual in the practical mathematician. The book contains the customary history of the development of statics, with full references to the original sources consulted. In this respect the volume would not be more than a somewhat enlarged version of the charming treatise of Mach on a similar subject. Duhem's book is animated by what seems to be a capital historical discovery. In the opening sections he states that *Rien ne nous laissait soupçonner que l'ensemble même de l'histoire de la Statique pût être bouleversé par nos recherches.* Such, however, is the case in Duhem's exhumation of Jordanus Nemorarius. With this philosopher the fundamental proposition that the same work is needed to raise different weights, if these are in the inverse ratio to the lifts applied, seems to have originated; and Duhem points out that the idea thus sown was gradually developed by the disciples of Jordanus Nemorarius, by Leonardo Da Vinci, by Cardanus, by Roberval, Descartes, Wallace, Bernoulli, to obtain its supreme interpretation in the work of Lagrange and of Willard Gibbs. *Carl Barus.*

Physikalisch-chemische Mineralogie. *By C. Doelter. (Handbuch der angewandten physikalischen Chimie. Herausgegeben von Prof. Dr. G. Bredig). Band II. 16 × 25 cm; pp. xi + 272. Leipzig: Johann Ambrosius Barth, 1905. Price: paper, 12 marks; bound, 13 marks.*—The subject is treated under the general headings: solid state; flowing crystals; size of the crystal molecule; polymorphism; isomorphism; morphotropism; relation between crystal form and chemical composition; relation between hardness and chemical composition of minerals; melting-points and heats of fusion of rock-forming minerals; nature of silicate melts; rate of crystallization; behavior of fused silicates; differentiation of silicates; volcanic magma; formation of crystalline slates; sublimation; zeolites and hydrates; aqueous solutions; growth of crystals; natural solutions of minerals; solubility and formation of minerals. This makes a most interesting volume though its value is chiefly suggestive. Very little exact work has been done in this field and the applications of physical chemistry are chiefly to come. When they do come, it will be the phase rule and not the theory of dilute solutions which will be the most helpful, a point which has not been fully grasped by the author.

In considering this book we must keep in mind that it has been written by a man who is not primarily a physical chemist and who is therefore often more

familiar with the form of physical chemistry rather than with its substance. This was inevitable because no physical chemist knows enough to write a book like this. On the other hand, it would add greatly to the value of this series if some physical chemist, presumably the editor, would look over the manuscript and cut out misleading or inaccurate statements.

Since an amorphous substance has no true melting-point, a table of melting-points, p. 9, should not be given without comment. One would like to know the evidence for the statement, p. 47, that substances forming a continuous series of solid solutions are not necessarily isomorphous. If a compound crystallizes from a melt at a certain temperature, it must be possible to make that substance by heating the dry components at that temperature, provided we are dealing with a reversible equilibrium. This has been overlooked, p. 115. On p. 127 the author states that fused silicates do not behave like alloys because the addition of one component does not necessarily lower the freezing-point of the other. This point was straightened out by van't Hoff fifteen years ago. The freezing-point curves, pp. 132–134 do not show the quadruple points which must exist and the discussion of the crystallization is not clear. It is hardly worth while, p. 135, to talk about the change of solubility in fused salts, due to the presence of a common ion when we know that these salts are miscible in all proportions when melted. On pp. 153–154 we have two pressure-temperature diagrams with the pressures measured along the abscissas in the first and along the ordinates in the second. It is inaccurate to say, p. 181, that hydrated salts are more soluble than the corresponding anhydrous salts Over the temperature range for which the hydrated salt is stable, the anhydrous salt is the more soluble. On p. 222 the author thinks that mixtures of fused salts are perhaps not solutions because they do not necessarily follow the law of van't Hoff-Raoult. This is putting the cart before the horse with a vengeance. On p. 55 the author decides that the experimental evidence is against diffusion in solids. It must be remembered that the rate of diffusion varies enormously with the temperature. Below 150° for instance it takes a very long time for alloys to reach equilibrium even when the components are intimately mixed. With minerals at ordinary temperatures the effect would be very much less marked. The reviewer feels quite certain that diffusion between minerals capable of forming solid solutions can be shown if the experiments are conducted under favorable conditions.

Wilder D. Bancroft.

Die Elektrolyse geschmolzener Salze. *Erster Teil. Verbindungen und Elemente. By Richard Lorenz. Monographien über angewandte Elektrochemie, XX. Band. 17 × 24 cm; pp. vi + 217. Halle: Wilhelm Knapp, 1905. Price: paper, 8 marks.*—This first volume deals chiefly with the qualitative side of the electrolysis of fused salts; and the quantitative relations are to be considered in a subsequent volume. The headings of the chapters are: the metals of the alkalies; the metals of the alkaline earths; aluminum and the rare earth metals; copper and silver; zinc, cadmium and mercury; germanium, tin and lead; arsenic, antimony and bismuth; vanadium, columbium and tantalum; selenium and tellurium; chromium, molybdenum, tungsten and uranium; manganese, iron, cobalt, nickel, gold and the platinum metals; the metalloids. This recapitulation shows how comprehensive the book is and the

text justifies the table of contents. Merely as a matter of historical interest the reviewer would have liked to have seen a reference to U. S. Patent 141,132 (1873) granted to Gauduin, Mignon and Rouart. So far as known this is the first recorded instance of fused cryolite being used as a solvent in an electrolytic bath. *Wilder D. Bancroft*

Thermodynamik und Kinetik der Körper. *By B. Weinstein. Dritter Band, erster Halbband: Die verdünnten Lösungen; die Dissociation; Thermodynamik der Elektricitat und des Magnetismus (erster Theil). 15 × 23 cm; pp. xvi + 464. Braunschweig: F. Vieweg und Sohn, 1905. Price: paper, 12 marks.*—Notices of the first and second volumes of Weinstein's comprehensive "Thermodynamics and Kinetics" may be found in this Journal, 5, 604, and 7, 591. The topics treated in the present first half of the third volume are, dilute solutions, dissociation, and the thermodynamics of electricity and magnetism. The second half of the third volume, to be devoted to electrolytic phenomena, will complete the work.

The present text begins with an exposition of van't Hoff's theory of dilute solutions, in which the limitations of the theory receive especial attention. This is followed by a general discussion of the physical properties of dilute solutions, including those involved in the equilibrium of osmotic processes. The theory of dissociation is next very carefully and extensively considered, and this portion of the volume is concluded by a chapter on the theory of the vapor-pressures and of the freezing temperatures of solutions. As in the preceding volumes, the treatment throughout is critical and constructive, and relevant experimental results are freely introduced.

The remainder of the volume, on the thermodynamics of electricity and magnetism, considers the theories of electric and magnetic phenomena, the measurement of electric and magnetic quantities, electrification and discharge, magnetization and demagnetization, the energy of electric currents and of magnets, the development of heat in electric circuits, thermocurrents, thermomagnetic and galvanomagnetic processes, and electromotive forces and contact electricity. *J. E. Trevor*

Die neuere Entwickelung der Kristallographie. *By H. Baumhauer. (Die Wissenschaft. Heft 7). 14 × 22 cm; pp. viii + 184. Braunschweig: Friedrich Vieweg und Sohn, 1905. Price: paper, 4 marks: bound, 4.60 marks.*—This small book is the seventh number of a series of monographs on natural science and mathematics issued by the above publishers. Besides an accurate and modern statement of the technicalities of crystallography, it presents a very brief summary of the more important methods, observations, and theories of recent date. Physical chemists may find especially interesting the discussion of "liquid crystals," and the chapters on the growth of crystals and on chemical crystallography. Solution or "etching" phenomena are treated—as one acquainted with the work of the author would expect—with an especially masterly touch.

As a whole, the book is too condensed for rapid comprehension by one who is not already rather familiar with the subject. *A. C. Gill.*

The New Knowledge. *By Robert Kennedy Duncan. 14 × 20 cm; pp. xviii + 263. New York: A. S. Barnes and Company, 1905. Price: cloth.*

$2.00 net.—In an enthusiastic manner the author presents a popularized summary of much of the recent work on conduction in gases and on radio-activity. The book evidently comes down to June, 1904, in regard to some of the literature; but it equally evidently does not come down to September of that year. A good deal of the dramatic effect would otherwise have been lost. There is no longer any evidence that a general transmutation of the elements is any more probable now than at any other time. It is probable that radium is formed in some way from uranium. We know that what we call radium breaks down and that helium is one of the final decomposition products. There is reason to believe that radio-active thorium, radio-active lead, radio-active tellurium, and radio-active bismuth are probably these metals with one or more of the decomposition products of radium condensed upon them. While this is most interesting, it is not at all analogous to the conversion of lead into gold. It is also quite inaccurate to say that thorium has just as much right to be considered an element as any other.

The author's statement that the law of the conservation of energy is liable to go by the board cannot be justified. Before the discovery of the emanation, it looked as though energy were being supplied from nowhere; but the moment we postulate the disintegration of radium, there is no longer any evidence that the law of the conservation of energy does not hold absolutely. Mr. Duncan is welcome to one set of thrills but he cannot have both.

While one cannot say that the book is well written, the style may be called sprightly. The unscientific reader will probably be more impressed by the parts that are wrong than by those that are right, but this will not be a very serious matter and he will at least be interested. *Wilder D. Bancroft*

Explication mécanique de la Matière, de l'Electricité, et du Magnétisme. *By M. Despaux. 14×23 cm; pp. 210. Paris: Félix Alcan, 1905.*—This book develops the idea that since electric, magnetic, and electromagnetic phenomena can be imitated by the behavior of rotating helical propellers in water or air, it follows that the appearance of these phenomena can be accounted for by the assumption that bodies are constituted of molecules having helical or other "propulsive forms." Forms of energy other than electric and magnetic are accounted for in like manner. *J. E. Trevor.*

Die physikalischen Eigenschaften der Seen. *By Otto Freiherr von und zu Aufsess. (Die Wissenschaft, Heft 4). 14×22 cm; pp. x + 120. Braunschweig: Friedrich Vieweg und Sohn, 1905. Price: paper, 3; bound, 3.60 marks.*—The present number of the *Wissenschaft* series of monographs is a clearly and simply written account of the physical properties of lakes, evidently designed to arouse the interest of the intelligent general reader rather than to edify the professional physicist. The phenomena considered are ordered on the plan of a treatise on physics, the successive chapters being concerned with phenomena of mechanics, sound, light, and heat. Under the heading mechanics are described ordinary wave motion, the standing waves that constitute seiches, and currents due to various causes. Under acoustics are treated the propagation of sound in water, and in air over the surface of a lake. Under optics we find a variety of information concerning the transparency of water, the phenomena due to reflection, refraction, dispersion, absorption, and polarization, and the

various shades of color that lakes assume under different conditions. Finally, under "thermics", the distribution of temperatures in lakes is discussed, and a few pages are devoted to the heat capacities of these bodies of water. The little book is entertainingly written, and should afford pleasure and profit to those who take a ready interest in what they see about them. *J. E. Trevor.*

Practical Measurements in Magnetism and Electricity. *By George A. Hoadley. 13 × 19 cm; pp. 111. New York: American Book Company, 1904. Price: bound, 75 cents.*—This book supplies directions for eighty-nine simple experiments in magnetism and electricity. These are intended to constitute a laboratory course preparatory for the study of electrical engineering. The experiments are arranged in a logical order, and each is accompanied by suggestive directions and by a simple discussion of the principles involved.

J. E. Trevor

Notes and Questions in Physics. *By John S. Shearer. 14 × 22 cm; vii + 284. New York: The Macmillan Company, 1904.*—This book is primarily a collection of problems in physics, accompanied by explanatory notes. All branches of the subject are involved, and typical problems are solved in the text. Nearly fifteen hundred problems being given, the same ground may be covered in class work for several successive years, using a different selection of problems each year. In devising the problems, the author has given considerable attention to graphical methods, especially to force diagrams, and he has not restricted himself to the C. G. S. system of units. The value of a book of this sort, for use in connection with a lecture course on physics, is beyond question; and the value of this particular book is enhanced by the circumstance that it is the outcome of an extended experience in the class-room. *J. E. Trevor.*

REVIEWS

The object of this department of the Journal is to issue, as promptly as possible, critical digests of all Journal articles that bear upon any phase of Physical Chemistry.

General

The elimination of thermometric lag and accidental loss of heat in calorimetry. *T. W. Richards, L. J. Henderson and G. S. Forbes. Proc. Am. Acad.*, 41, *3; Zeit. phys. Chem.*, 52, *551* (*1905*).—It is shown that the Beckmann thermometer does not follow the heat changes in calorimetric work with sufficient rapidity. To eliminate this and to cut off losses by radiation, the authors enclose the calorimeter in a jacket which is kept always at the same temperature as the liquid in the calorimeter. It seems to the reviewer that the use of a Dewar bulb as a calorimeter might have some advantages. While the authors have devised an interesting and accurate method, they do not give Waterman's method quite its proper due. *W. D. B.*

The relative value of calorimetric methods. *J. Thomsen. Zeit. phys. Chem.* 53, *314* (*1905*).—A further criticism of some of Berthelot's data (Cf. 9, 711). *W. D. B.*

Calorimetric measurements of heats of combustion. *W. Jaeger and H. v. Steinwehr. Zeit. phys. Chem.* 53, *153* (*1905*).—A description of the method of calibrating the Berthelot bomb. *W. D. B.*

On the velocity of sound in very small tubes. *F. A. Schulze. Drude's Ann.* 13, *1060* (*1904*).—The Quincke interference tubes were used with glass, rubber, and brass tubes from 1 to 1½ millimeters bore. A tuning fork or a tin whistle supplied the source of sound. An accuracy of about 2 percent was attained. The velocity was found to range from 189 meters per second to 290. Dry air free from CO_2 was used in the experiments and the nature of the tube was found to exert a marked influence. *H. T. B.*

One-Component Systems

Deduction of some familiar formulas from a general equation of state. *G. van Iterson, Jr. Zeit. phys. Chem.*, 53, *633* (*1905*).—A discussion of the special formulas coming under the general equation

$$F(p, v, T, a, b, c) = 0$$

where the form of the function is the same for all substances, while a, b and c are mutually independent constants, varying with each substance. *W. D. B.*

Amorphous sulphur. II. *A. Smith, W. B. Holmes and E. S. Hall. Zeit. phys. Chem.* 52, *602* (*1905*).—Reviewed (9, 595) from Jour. Am. Chem. Soc. 27, 797 (1905). *W. D. B.*

On the vapor pressure of water at high temperatures. *C. Dielerici. Drude's Ann.*, **13**, *860* (*1904*).—The author deduces a logarithmic expression for the pressure as a function of the temperature which is similar to the formula of van der Waals deduced from the theory of corresponding states. It is shown that the equation represents well the experimental results up to the critical temperature. *H. T. B.*

Investigations of critical density. *G. Teichner. Drude's Ann.* **13**, *595* (*1904*).—The author studies the identity of liquid and vapor around the critical point, the liquid used being carbon tetrachloride. The temperature was found to be very variable at which it could be said that the difference in density no longer existed. A number of beads of varying density were placed in the tube containing the liquid, and formed the basis of observation. It is shown that greater variations in density occur than could be accounted for by unequal temperature distribution in the tube. He suggests that the explanation may be found in the Kinetic Theory. *H. T. B.*

Remark on the critical temperature of water and mercury. *J. Traube and G. Teichner. Drude's Ann.*, *13*, *620* (*1904*).—Water was enclosed in a quartz tube and heated. The meniscus was found to disappear at 374° and to reappear at the same point. Similar experiments with mercury in a closed tube gave less positive results, but the critical point was found to be around 1000°. *H. T. B.*

Investigations of the critical heat of vaporization. *G. Teichner. Drude's Ann.* **13**, *611* (*1904*).—The author determines the total heat required to raise a quantity of ether contained in a closed tube from 17° up to and above the critical temperature. The plotted curves intersect at 191°. Calorimetric measurements were made of the heat. *H. T. B.*

The calorimetric measurements of liquid oxygen and nitrogen. *H. Alt. Drude's Ann.*, **13**, *1010* (*1904*).—The heat of vaporization and the specific heat of both liquid O_2 and liquid N_2 are determined. The first by heating with an electric spiral and the second after allowing for the rate of heat absorption from the outside by suddenly changing from a low pressure to atmospheric pressure, and measuring the heat necessary to bring the liquid up to the temperature corresponding to the higher pressure. It is found that the heat of vaporization of O_2 changes rapidly with the temperature. In the case of N_2 it is a linear function of the temperature, but not so with O_2. The specific heat of O_2 between —200° and —183° is found to be 0.347 ± 0.014 and for N_2 between —208° and —196°, 0.430 ± 0.008. *H. T. B.*

Compressibility of gases between one atmosphere and half an atmosphere pressure. *Lord Rayleigh. Zeit. phys. Chem.*, **52**, *705* (*1905*).—This paper covers the same ground as the preceding (8, 137) but gives more details. From density determinations under diminished pressure the following atomic weights are deduced: hydrogen, 1.0086; carbon, 12.003; nitrogen, 14.003. *W. D. B.*

Two-Component Systems

Alloys of magnesium with tin and lead. *N. S. Kurnakow and N. J. Stepanow. Zeit. anorg. Chem.*, **46**, *177* (*1905*).—The authors suggest the adoption of

the term *metallide* to describe the well-defined intermetallic compounds, and thus come out with terms plumbide, mercuride, cupride. By combination, one obtains tricuprostibnide and potassium dimercuride, or inversely, antimonytricupride or dimercury potasside. Considering the magnesium compounds with lead and tin as derivatives of the MH_4, where M represents either tin or lead, the authors find dimagnesiumstannide and dimagnesiumplumbide. This nomenclature may be desirable, or it may not. It ranks with the use of specific names for the hydrated salts, and while there is no objection to it, there is no very great advantage in the names suggested.

The freezing-point curves were determined for mixtures of tin with magnesium and lead with magnesium, and were found to consist each of four branches. The addition of magnesium to tin lowers the freezing-point in accordance with the van't Hoff formula, thus indicating the absence of solid solutions, a fact which is borne out by the presence of eutectic over this branch of the curve. The atomic depression found was 3.0 ± 0.1, thus agreeing very closely with the theoretical value of 3.0. Similarly, the addition of magnesium to lead lowers the freezing-point, but in this case the atomic depression is 4.4 instead of 6.5 calculated by the formula. But the presence of the eutectic in these concentrations shows that this variation from the calculated value is not due to solid solutions. It is to be noted that in one case the theory applies and in the other it does not, the conclusions being identical in both cases. There is a maximum in the curve for tin and magnesium located at the composition Mg_2Sn, temperature being 795. The two eutectics for this series lie at 8.5 atomic percents of magnesium —203.5°, and at 88 atomic percents of magnesium —580°.

The maximum in the lead magnesium series is at Mg_2Pb, 550°, the two eutectics being 15.73 atomic percents —253° and 80 atomic percents —475°.

The dimagnesiumstannide is a steel gray color, showing octahedral cleavage of which the angles were found to be 70° 33′. The density of this compound is 3.591. The hardness is 3.5, being thus considerably greater than that of either of the components.

Moist air decomposes both of these compounds and most of the alloys, yielding in the one case metallic tin and magnesium hydroxide, and in the other case a mixture of basic magnesium and lead hydroxides, apparently the same product as that found by Grube. Twelve photomicrographs accompany the paper and the authors agree with Grube that the melting-point of magnesium is at 650° instead of 635°. *E. S. S.*

Tellurium-bismuth alloys. *K. Mönkemeyer. Zeit. anorg. Chem.*, 46, *415* (*1905*).—The author finds a maximum in the curve indicating the compound Bi_2Te_3. The melting-point of this compound is 573°, over 100° above the melting-point of either of the components. The eutectic between bismuth and the compound lies at 99 percent and 261°. The eutectic between the compound and tellurium lies at 13.9 percent bismuth and 388°. The melting-point of the tellurium used was 428°. There seems to be no evidence of the formation of solid solutions. The sections were etched with dilute nitric acid and with copper ammonium chloride. *E. S. S.*

Manganese-iron alloys. *M. Levin and G. Tammann. Zeit. anorg. Chem.*, 47, *136* (*1905*).—It was found necessary to examine these alloys in an atmos-

phere of hydrogen, and no particular accuracy is claimed for the work, a certain amount of change of composition being unavoidable. The freezing-point curve determined is more or less continuous from that of manganese to that of iron. It possesses a marked inflection, but the authors are of the opinion that the components form a complete series of isomorphous mixtures at high temperatures. The curve given is corrected, using the Tammann interpolation formula correcting for superheating and supercooling, and for reasons indicated in a previous review, can be regarded as only approximate. It was found that there was a marked difference in the appearance of the alloys when quenched from high temperatures and when allowed to cool slowly. No attempt was made to determine the equilibrium diagram and the paper goes little further than to show that the components melt together in all proportions, and that the freezing-point curve indicates a continuous series of solid solutions. *E. S. S.*

The phenomena which occur in a binary mixture when the plait-curve meets the solubility curve. *A. Smits. Zeit. phys. Chem.*, 52, 587 (*1905*).—This paper contains the quantitative data in detail for the equilibrium between anthraquinone and ether (8, 137). *W. D. B.*

On the change in volume taking place in phase-changes of binary mixtures. *R. Hollman. Drude's Ann.*, 13, 325 (*1904*).—It is shown that the volume change for binary mixtures can be expressed by a differential equation which is represented qualitatively by a mixture of $Na_2(Cr,S)O_4.10Aq$. From the volume and entropy relations for change of phase in these mixtures a critical point in the change from crystal to liquid does not exist. *H. T. B.*

A remark to the paper by Hollman on the change in volume by the phase-change in binary mixtures. *S. Schaibe. Drude's Ann.*, 13, 1076 (*1904*).—The author shows that the mathematical treatment of the subject by Hollman (see preceding review) is unnecessarily complicated, and proceeds to show a simpler method of treatment. *H. T. B.*

On colloid solutions. *C. Benedicks. Zeit. phys. Chem.*, 52, 733 (*1905*).—When martensite breaks down into pearlite, there is an intermediate structure to which the name of troostite has been given. The author suggests considering troostite as a colloidal solution. The mere fact that it is not a colloidal solution does not trouble him in the slightest. *W. D. B.*

A modification of the van't Hoff theory of the lowering of the freezing-point. *J. B. Goebel. Zeit. phys. Chem.*, 53, 213 (*1905*).—The author shows that the heat of sublimation of ice and therefore the heat of fusion are not independent of the temperature. He introduces a correction for this in the formula for the molecular lowering of the freezing-point. *W. D. B.*

Lecture experiments to show solid solutions. *E. Beckmann. Zeit. phys. Chem.*, 53, 151 (*1905*).—Solutions of iodine in benzene and in *p*-xylene are allowed to freeze and are then placed in a centrifugal machine. The solid *o*-xylene comes out nearly colorless while the solid benzene is dark red. *W. D. B.*

On the influence of temperature and pressure on the absorption and diffusion of hydrogen through palladium. *G. N. S. Schmidt. Drude's Ann.*, 13, 747

(*1904*).—It is found that above 140°, the absorption increases with the pressure and diminishes with the temperature. The diffusion increases both with the pressure and temperature. Under 140° the results are irregular. A large number of tables and curves are given. *H. T. B.*

Iron and chromium nitrides. *E. Baur and G. L. Voerman. Zeit. phys. Chem.*, 52, *467* (*1905*).—No nitride of iron, Fe_4N, could be formed even by passing the nitrogen under fourteen atmospheres pressure over heated iron. No definite dissociation pressure could be obtained for the nitride of chromium because there seemed to be a time factor. There is also some reason to believe that chromium and chromium nitride form solid solutions.

While chromium nitride is an excellent catalytic agent for the decomposition of ammonia, it appears not to accelerate the reverse reaction in the slightest. This is of course difficult to understand if one insists that a catalytic agent cannot displace the equilibrium. *W. D. B.*

The application of the vapor-heating method for determining molecular weights at high temperature. *E. Beckmann. Zeit. phys. Chem.*, 53, *137* (*1905*).—The author finds that vapor heating gives too high values of the boiling-point with low boiling liquids and too low values with high boiling liquids. He claims that the method of direct heating with a flame gives the most accurate results. This would be more convincing if it were not for Beckmann's failure to notice work which controverts this. *W. D. B.*

Determination of molecular weights in concentrated boiling sulphuric acid. *E. Beckman. Zeit. phys. Chem.*, 53, *129* (*1905*).—A modification of the familiar boiling-point apparatus is described, which makes determinations possible with concentrated sulphuric acid as solvent. Assuming that boric and arsenious anhydrides are to be represented by the formulas B_4O_6 and As_4O_6 respectively, the author obtains a constant of 53.3 while 58.2 is the value calculated from the heat of vaporization. Molybdanic anhydride gives values of the molecular weight corresponding to the formula Mo_3O_8. Sodium and potassium pyrosulphates gave values agreeing with the formula weights. With sodium and potassium sulphates the observed molecular weights were lower than the formula weights, while with potassium bisulphate they were much higher. The author attempts to explain both variations by assuming the formation of pyrosulphates.

W. D. B.

The properties of mixtures of nitric and sulphuric acids. *A. Saposchnikow. Zeit. phys. Chem.*, 53, *225* (*1905*).—This paper contains data on the vapor-pressures and vapor compositions of mixtures of nitric acid (sp. gr. 1.40) with sulphuric acid, and also data on the effect of slight additions of water. From these results and from those in the preceding papers (9, 339, 717) it is clear that addition of sulphuric acid is necessary when nitrating substances in order to prevent a lowering of the vapor-pressure of the nitric acid by the water formed during the reaction. *W. D. B.*

Studies on aqueous solutions of aliphatic acids. *K. Drucker. Zeit. phys. Chem.*, 52, *641* (*1905*).—The author has determined the conductivity, the surface tension, the specific volume, and the compressibility for aqueous solutions of

aliphatic acids. He then calculates the true and the apparent critical data, and also the internal pressure. The discussion of the results led to nothing interesting. *W. D. B.*

Hydration, color and the formation of complexes. *F. G. Donnan. Zeit. phys. Chem.*, 53, *317* (*1905*).—The author criticizes the papers of Lewis (9, 717) and of Jones and Bassett (9, 715) as not representing the scientific knowledge of to-day. He points out that the work of Werner, of Abegg and Bodländer, of Kohlschütter, and of Fox, Bassett and Dawson has been overlooked. *W. D. B.*

Multi-Component Systems

Reciprocal salt pairs. IV. *W Meyerhoffer. Zeit. phys. Chem.*, 53, *513* (*1905*).—At all temperatures barium carbonate and potassium sulphate are the stable pair. It is shown that the ratio of potassium sulphate to potassium carbonate in the solution is not constant and that the conclusions of Guldberg and Waage were made possible only by an unconscious weeding out of all contradictory data, by not having allowed the solutions to reach equilibrium, and by an inaccurate method of analysis. The experiments of Dulong, Rose, Debus and others are discussed in detail. It was noticed that freshly-precipitated barium sulphate has a temporary power of absorbing potassium sulphate. *W. D. B.*

Solubility relations for analogous double salts. *J. Koppel. Zeit. phys. Chem.*, 52, *385* (*1905*).—Solubility determinations were made for the double salts of sodium sulphate with the sulphates of cobalt, nickel, iron, zinc, cadmium and magnesium. The discussion of general relations does not seem to the reviewer to have led to any practical results. *W. D. B.*

Inversion relations of polymorphous substances. *H. Steinmetz. Zeit. phys. Chem.*, 52, *449* (*1905*).—The author has determined inversion-points for sodium magnesium uranyl acetate and isopropyl ammonium platinic chloride under different pressures. *W. D. B.*

Absorption of carbon dioxide by aqueous salt solutions and mixtures of two liquids. *A. Christoff. Zeit. phys. Chem.*, 53, *321* (*1905*).—When carbon dioxide is more soluble in a mixture of two liquids than in either of the liquids, there is also a minimum surface-tension for some mixture. The minimum surface-tension as measured and the maximum solubility do not coincide. When no chemical reaction can take place, carbon dioxide is less soluble in a salt solution than in water. When a salt solution absorbs more carbon dioxide than pure water, the amount is not enough to change the whole of the salt into bicarbonate. *W. D. B.*

The physical chemistry of the toxine-antitoxine reaction with special reference to the neutralization of lysine by antilysine. *J. A. Craw. Zeit. phys. Chem.*, 52, *569* (*1905*).—The lysine in the filtrate from cultures of *Bacillus megatherium* is a fairly stable substance which resembles somewhat the tetanus lysine and the diphtheria toxine. This lysine diffuses through gelatine while the antilysine does not. Free lysine or free antilysine could be shown to occur in solutions containing an excess of the other. When antilysine is present in excess, the reaction appears to be reversible to some extent, though false equilibrium

seems to occur when lysine is present in excess. Since the equilibrium relations vary with the absolute concentration the author concludes that the views of Arrhenius and Madsen are incorrect. He looks upon the removal of lysine by antilysine as analogous to an absorption phenomenon. *W. D. B.*

Preparation of silicic acids by decomposing natural silicates. *G. Tschermak. Zeit. phys. Chem.*, 53, *349* (*1905*).—The author has decomposed a number of silicates with hydrochloric acid and has analyzed the resulting silicic acids. He believes that he has obtained the following acids already: H_4SiO_4, H_2SiO_3, $H_4Si_2O_6$, $H_4Si_3O_8$ and $H_2Si_3O_7$. In this way the author expects to determine the constitution of the natural silicates; but he does not discuss the sources of error as much as one could wish. *W. D. B.*

Osmotic Pressure and Diffusion

Diffusion coefficients in relation to the concentration determined by means of bent light rays. *F. Heimbrodt. Drude's Ann.*, 13, *1028* (*1904*).—The coefficient of free diffusion is determined to 0.42 percent, which is much better than previous results. Linear relations are shown for the change of diffusion coefficient with concentration, a decrease for NaCl and urea and an increase with HCl in the case of rising concentration. With glycerol the coefficient falls rapidly with strong concentrations. *H. T. B.*

Velocities

The rate of decomposition of nitrous oxide. *M. A. Hunter. Zeit. phys. Chem.*, 53, *441* (*1905*).—The rate of decomposition of nitrous oxide at 713°–895° shows that the reaction is of the second order, according to the equation $2N_2O = 2N_2 + O_2$. Presence of water vapor does not change the rate. The density was determined in a very ingenious way by placing a glass bulb, filled with air and drawn out to a capillary, on a knife edge and noting the displacement of the capillary pointer. *W. D. B.*

Reaction velocities at low temperatures. *J. Plotnikow. Zeit. phys. Chem.*, 53, *605* (*1905*).—The reaction between ethylene and bromine in petroleum ether as solvent is of the second order at temperatures between —78° and —100°. The course of the reaction was followed by noting the concentration in volume. The temperature coefficient per 10° is 6.2. Ethylene from different sources appeared to react with very different rates; but this was not followed out. The unfortunate result of this is that the temperature coefficient was determined from experiments in which the reaction velocity constant was only about one-tenth what it was in the experiments to determine what the order was. *W. D. B.*

Heterogeneous catalytic reactions. *M. Bodenstein and F. Ohlmer. Zeit. phys. Chem.*, 53, *166* (*1905*).—It was found that the reaction between carbon monoxide and oxygen is accelerated by quartz and that carbon monoxide apparently acts as a negative catalyzer, checking its own combustion. This last effect is so marked that the reaction velocity varies inversely proportionally to the concentration of carbon monoxide. While this is very interesting, it would seem to make conclusions based on reaction velocity experiments even more unsatisfactory than they usually are. *W. D. B.*

The platinum catalysis of hydrogen peroxide as a diffusion phenomenon. *G. Senter. Zeit. phys. Chem.*, 52, *736* (*1905*).—"It is shown that the variations from the simple logarithmic formula, in the catalytic decomposition of hydrogen peroxide by colloidal platinum, are probably due to disturbances caused by convection currents. It is also shown that an increased convection cannot have much effect on the reaction velocity when the velocity constant as calculated from Nernst's diffusion hypothesis is large in comparison with the chemical velocity constant." *W. D. B.*

Electromotive Forces

The theory of reversible galvanic cells. *A. Denizot. Drude's Ann.*, 13, *193* (*1904*).—Starting with the well-known equation of Helmholtz the author develops what he calls an electrochemical scale of absolute temperature. It is shown that for a reversible cell the ratio of the electrical energy and heat developed at the zero of the conventional scale to the temperature coefficients is constant. Also that the ratio of the differences of the same to the thermal coefficients is constant, and the ratio of the electrical to the thermal coefficients is constant. Values for the various constants can be obtained by a comparison of the scale with the thermodynamic scale. *H. T. B.*

Effect of solvent on the equilibrium constant. *L. Pissarjewsky and N. Lemcke. Zeit. phys. Chem.*, 52, *479* (*1905*).—The author finds that the equilibrium $2KCl + Hg_2SO_4 \rightleftharpoons Hg_2Cl_2 + K_2SO_4$ depends on the nature of the solvent. Electromotive force measurements were made with water, water plus alcohol, and water plus glycerol as solvents. For 0.01 *n* solutions the electromotive force was 0.305 volt in aqueous glycerol solution, 0.301 volt in aqueous alcohol, and 0.298 volt in water. The authors find extraordinary fluctuations with changing concentration for the viscosity of sodium chloride dissolved in various solvents. It is scarcely probable that these viscosity determinations can represent anything more than experimental error. *W. D. B.*

The elimination of the potential difference between two dilute aqueous solutions by means of a concentrated potassium chloride solution. *N. Bjerrum. Zeit. phys. Chem.*, 53, *428* (*1905*).—The author argues that the introduction of a concentrated potassium chloride solution between any two aqueous solutions eliminates the potential difference. It is difficult to see how this can be the case and the author's proof of it is not convincing. *W. D. B.*

Comment on Fischer's paper "On the chemical transference of potentials." *R. Luther. Zeit. phys. Chem.*, 52, *626* (*1905*).—It is pointed out that most of Fischer's conclusions (9, 721) had been published in 1901 by the author. *W. D. B.*

On the electrocapillary movements and a current in an open cell. *J. Billitzer. Drude's Ann.*, 13, *827* (*1904*).—It is found that mercury falling in drops through a column of water containing an electrolyte causes a difference of potential between upper and lower levels sufficient to cause a current in an external circuit. The phenomenon is investigated very carefully. The size of the potential difference is of the order of one hundredth of a volt. *H. T. B.*

The theory of the residual current. *W. Nernst and E. S. Merriam. Zeit. phys. Chem.*, 53, 235 (1905).—The residual current was studied, using one large stationary electrode and one small one which was rotated rapidly. With a good depolarizer the problem becomes simply one of diffusion. When the depolarizer reacts slowly, the residual current becomes less and the effect of the rate of stirring decreases. *W. D. B.*

Comparison of the platinum thermometer with the normal thermometer between 444° and −190° C. *M. W. Travers and A. G. C. Gwyer. Zeit. phys. Chem.*, 52, 437 (1905).—The relation between the resistance thermometer and the gas thermometer can be expressed satisfactorily by a parabolic equation between −190° and 0°; but it is not the same formula which expresses the relation between 0 and 444°, the value for δ being 1.90 in the first case and 1.50 in the second. Neither formula can be used for extrapolation. *W. D. B.*

Effect of alternating currents on the mean potential of electrodes. *P. G. Gundry. Zeit. phys. Chem.*, 53, 177 (1905).—The author has studied the effect of an alternating current on one large and one small mercury electrode. Two phenomena may be observed. Owing to the asymmetry of the polarization there may be an apparent dilution in the neighborhood of the large electrode. If part of the cathodic current is carried by hydrogen there may be an actual increase in the concentration of mercury as ion near the large electrode. When no complex salts are formed, the second phenomenon masks the first. With complex salts the second phenomenon does not occur and the first can then be readily detected. *W. D. B.*

An automatic potential regulator. *A. W. Gray. Drude's Ann.*, 15, 607 (1904).—A device for automatically regulating potentials with an influence machine from 5000 volts up. It is to be used in place of the point discharge. *H. T. B.*

Electrolysis and Electrolytic Dissociation

Ionic sizes in relation to the conductivity of electrolytes. *W. R. Bousfield. Zeit. phys. Chem.*, 53, 257 (1905).—The author points out that all the modifications of the dilution law become possible if we assume hydrated ions and hydrated and polymerized undissociated salts. While this is quite true, it does not follow at all that this is the true explanation. In order to satisfy all the requirements the author postulates the existence of $NaOH.20H_2O$ in solution at 0° and a higher degree of hydration at 40°. The reasoning throughout the paper is very ingenious and the article is well worth reading. To the reviewer it seems a triumph of formalism. Of what real use is it to calculate values which we know to be wrong? Until we have some method of determining the percentage dissociation of a strong electrolyte, it is rather a waste of time to speculate as to the form of the dilution law. *W. D. B.*

Conductivity and dielectric constant of some substances below and in the critical condition. *P. Eversheim. Drude's Ann.*, 13, 492 (1904).—Resistance-temperature curves for ammonia, sulphur dioxide, and a solution of copper nitrate in ammonia were taken. Three curves in each case were plotted: one for the liquid continuously shaken; one for the liquid layer quiet; and one for the vapor layer.

Similar results for the dielectric constant are obtained for H_2S, for chlorine and for ether. No abrupt break occurs in the curves at the critical temperature. *H. T. B.*

Dielectricity and Optics

The influence of cathode rays on solid dielectrics. *A. Becker. Drude's Ann.*, 13, *394* (*1904*).—From the author's previous work it was shown that a dielectric under the influence of radium rays showed a slight increase of conducting power. In the present paper the effect of cathode rays is tried, which seems to show somewhat similar results. The effects are very small and somewhat uncertain. Paraffin formed the inner layer of a small condenser in metal plates, one of which is aluminium. *H. T. B.*

Research on electrolytic wave detection. *V. Rothmund and A. Lessing. Drude's Ann.*, 15, *193* (*1904*).—A careful study is made of the decomposition cell with a thin platinum point as electrode to be used as a detection for electric waves. An electrolyte of dilute sulphuric acid was used. The effect of the waves is to increase the current through the cell and diminish the potential of polarization. The effect is equally good with the platinum point as anode or cathode and is not connected with a distinct chemical change. The sensitiveness increases with the polarizability of the electrode point. The explanation offered by the author is that the effect of the waves is one of depolarization. *H. T. B.*

On the application of the electrolytic detecter in bridge measurements. *W. Nernst and F. von Lerch. Drude's Ann.*, 15, *836* (*1904*).—The detecter consists of two platinum electrodes in dilute sulphuric acid or caustic potash. One of the electrodes is very small, made from 0.02 mm wire. A polarizing current of 2 volts is used. Accurate results can be obtained with high frequency currents using a telephone or galvanometer. *H. T. B.*

The positive electrons and the existence of higher atomic weights. *W. Wien. Drude's Ann.*, 13, *669* (*1904*).—As an explanation of the author's previous results showing the existence of positive electrons with differing specific charges, J. Stark offered his theory that only electrons of one specific charge exist, but the variable results were due to the neutralizing influences of combining negative electrons. The author finds, however, after careful tests, that this theory is untenable.

On the view of higher atomic weights he finds the value of E/m as high as 15.5, which corresponds to a molecular weight of 650. *H. T. B.*

On the radio-active emanation in water and oil springs. *F. Himstedt. Drude's Ann.*, 13, *573* (*1904*).—This is a very complete study of the occurrence of an emanation in nature. It appears to be identical with the radium emanation. *H. T. B.*

On the action of the canal rays on aluminum and zinc oxide. *G. C. Schmidt. Drude's Ann.*, 13, *622* (*1904*).—This is a reply to a criticism of the author's previous work by J. Tafel. It is found that aluminium and zinc oxides in absolute purity do not fluoresce but only if they contain other oxides as a solid solution. Tafel maintained that the fluorescence was due to a physical change occasioned by local pressure. *H. T. B.*

Ozonization by the silent electric discharge. *E. Warburg. Drude's Ann.*, 13, *464* (*1904*).—The ozone is produced by the discharge in a current of oxygen and is estimated by passing it into a standard solution of sodium arsenate. The quantity of ozone formed by one coulomb from a metal point was determined using different earthed electrodes. It was found that the quantity was independent of the electrodes. Positive electrification gave the best results. It was shown that the ozone can be ascribed only to chemical action of the ultra-violet or to cathode rays and not to an electrolytic action. *H. T. B.*

On the ozonization of oxygen by the silent electric discharge. *A. W. Gray. Drude's Ann.*, 13, *477* (*1904*).—A study is made of the amount of ozone produced per coulomb of electricity in a Siemens' tube. The quantity was found to be independent of the potential difference between the coatings of the jar and probably also of the strength of the current. The most economical production is when the potential is just great enough to cause a discharge to pass.

H. T. B.

On spontaneous deozonizing. *E. Warburg. Drude's Ann.*, 13, *1080* (*1904*). —The author corrects an arithmetical mistake in a previous paper. *H. T. B*

On the formation of helium from the radium emanation. *F. Himstedt and G. Meyer. Drude's Ann.*, 15, *184* (*1904*).—The authors repeat Ramsay and Soddy's experiment. The emanation from 50 mg of radium bromide was condensed in a tube having aluminum electrodes by passing a current of hydrogen over the heated salt. The tube was exhausted and sealed while still cold. Not until four months were the helium lines visible. The authors attribute the slow result to the presence in the tube of the hydrogen. They next tried an electrodeless quartz tube, using radium sulphate and heating the salt in the exhausted tube. For three days no helium was visible; at the end of three weeks, however, the lines appeared. The authors express no definite opinion as to whether the helium was occluded in the radium salt in this case or produced from the emanation.

H. T. B.

Reversible photochemical reactions in a homogeneous system. II. *R. Luther and F. Weigert. Zeit. phys. Chem.*, 53, *385* (*1905*).—This is a continuation of the previous paper on the equilibrium between anthracene and dianthracene (9, 726). The reaction velocity varies with the nature of the solvent as well as with the temperature. A discussion of the mechanism of the reaction led to no result because all the facts could be explained fairly satisfactorily by two different hypotheses. Incidentally it was found that the reaction between chlorine and benzene is more complicated than had been assumed by Slator (8, 373).

W. D. B.

The color of lakes. *Otto, Freiherr v. u. z. Aufsess. Drude's Ann.*, 13, *678* (*1904*).—This is a careful study of the natural color of the Bavarian lakes. Ordinary daylight was used, and a spectro-photometric examination was made, using a Nernst lamp. There are some new views expressed as regards the causes influencing the color. After describing his apparatus the author discusses the color of pure water and water containing impurities, comparing this with lake water.

The effect of temperature on the color is treated and it is found that the temperature has no effect on the color. The diffraction theory of Rayleigh is contrasted with the author's chemical theory to the advantage of the latter. The color is considered due to the chemical composition of the water. *H. T. B.*

On the relation between pressure and refractive index of gases at pressures under one atmosphere. *W. Kaiser. Drude's Ann.*, 13, *210* (*1904*).—Since the work of previous observers on the behavior of various gases to Boyle's law for low pressures is not concordant, an attempt is made to study the subject by another method. The relation between $(n - 1)$ and the density being fairly well known the relation between the refractive index "n" and pressure is obtained. *H. T. B.*

On the cause of the color changes in gold-gelatine preparations. *F. Kirchner and R. Zsigmondy. Drude's Ann.*, 15, *573* (*1904*).—It is shown that the red color of colloidal gold solutions in water is not altered by the addition of gelatine, albumen, sugar, or salt, although a change in refractive index results, provided the mean distance between the particles remains the same. Changes of color to blue or violet take place when the particles come near together, much as would be produced by drying pieces of gold-gelatine. The author shows that his results are supported by Planck's theory. *H. T. B.*

The application of the thermopile in the ultra-violet and the energy distribution in the spark spectrum of metals. *A. Pflüger. Drude's Ann.*, 13, *890* (*1904*).—The author shows how the thermopile may be successfully used in the ultra-violet region. The spark spectra for numerous metals from 186 $\mu\mu$ to 233 $\mu\mu$ are given. Experiments with a Rowland grating are made from Al, Ni, and Cd. The influence of the experimental conditions on the rays, such as spark length, is discussed. A description is given of a simple method for demonstrating the thermal effect of the ultra-violet rays. *H. T. B.*

The ultra-violet spark and band spectrum of sulphur. *J. M. Eder and E. Valenta. Drude's Ann.*, 13, *640* (*1904*).—The present note is a remark to a paper by G. Berndt on the ultra-violet spark spectrum of selenium. Berndt considered that he was unable to obtain the spectrum free from sulphur lines. The authors study the sulphur spectrum carefully and find that there is only one line near the suspected impurity of Berndt. They therefore conclude that the selenium spectrum of Berndt was free from sulphur lines. *H. T. B.*

Remark to the paper by Eder and Valenta on the ultra-violet spark and band spectrum of sulphur. *G. Berndt. Drude's Ann.*, 13, *1078* (*1904*).—In spite of the criticism offered by Eder and Valenta (see preceding review) the author insists that no wave-length measurements exist in the ultra-violet and he was hence unable to compare his selenium spectrum with that of sulphur in this region. *H. T. B.*

On the dark strips appearing in the overlapping spectra produced by Lippmann's method of photography. *L. Pfaundler. Drude's Ann.*, 15, *371* (*1904*).—A careful study of what the author calls Zenker's strips which appear in overlapping spectra produced by Lippmann's photographic method. They appear to be long, dark, parallel bands traversing the spectra. *H. T. B.*

Production of bubbles, lattice forms and mother of pearl colors by illuminating bichromated gelatine, silicic acid, albumen, etc. *G. Quincke. Drude's Ann.*, 13 65 (*1904*).—A continuation of a long series of articles by the author. The present papers deal with the production of liquid precipitates by the action of light. *H. T. B.*

Studies on chemiluminescence. *M. Trautz. Zeit. phys. Chem.*, 53, *1* (*1905*). The author has made an enormous number of experiments on substances which emit light when crystallizing or when reacting. As is not surprising, he finds these phenomena much more wide-spread than was commonly supposed. Crystalloluminescence is apparently always a case of triboluminescence but the author is forced to leave the matter there. As regards chemiluminescence about the only point established is that the intensity of the light is usually increased by an increase in reaction velocity. The paper is hard reading because the author uses abbreviations under all circumstances, even in the summary of results. Merely as one instance the unfortunate reader has to hark back from p. 95 to p. 4 to find out what the mystic symbols 'R.L.' denote. *W. D. B.*

The phenomenon of phosphorescence. *A. Dahms. Drude's Ann.*, 13, *425* (*1904*).—The author studies the effect of heat rays in reducing phosphorescence. Under the action of the long light rays the glow increases before being extinguished. Rays from 3μ to ultra violet are employed in the investigation on plates of Balmain's paint, strontium and zinc sulphides and fluorspar. The plates were made phosphorescent by white light and then on removal subjected to spectrum rays. A number of interesting results are obtained. *H. T. B.*

On the phosphorescence of the alkaline earths. *P. Lenard and V. Klatt. Drude's Ann.*, 15, *225*, *425*, *633* (*1904*).—These are papers of considerable magnitude which deal with a spectroscopic study of the phosphorescence of the alkaline metal salts alloyed with such metals as copper, manganese and bismuth. The whole research of which the papers form a part includes a study of some 800 preparations and 300 spectroscopic examinations. Analogies are found between lines of the metals in various alkaline sulphides and also between lines of different metals in the same sulphide. A comparison is made of the position of the lines in the spectrum, and a study made of the influence of the temperature on the mixture and on the form of excitation on the phosphorescence. *H. T. B.*

Crystalloluminescence and the triboluminescence. *M. Trautz. Zeit. Elektrochemie*, 11, *306* (*1905*).—All substances which give out light on crystallizing have also a temporary power of emitting light when the crystals are stirred. This disappears after a few days. *W. D. B.*

The light emitted by crystals of arsenious anhydride. *D. Gernez. Comptes rendus*, 140, *1134* (*1905*).—The author finds that no light is emitted when arsenious acid crystallizes from a hydrochloric acid solution; but that light is emitted when the crystals are crushed. It is therefore a case of triboluminescence. Experiments have shown that four months after precipitation light can be obtained from the crystals. *W. D. B.*

Triboluminescence of arsenious acid. *J. Guinchant. Comptes rendus*, 140, *1170* (*1905*).—The author agrees with Gernez (preceding review) as to the cause of the light from crystals of arsenious acid. The light itself has a relatively high photographic power and is essentially that of an incandescent solid. The author has observed that when urea is added to a concentrated hypochlorite or hypobromite solution there is a vivid luminescence. This light is poor in photochemical rays. The same effect can be produced with several other nitrogen compounds and is believed by the author to be due to the decomposition of nitrogen trichloride. The luminescent spectrum is identical with that given by nitrogen trichloride when decomposing explosively.

When sodium amalgam is thrown into a concentrated solution of sodium hypobromite, the bubbles of hydrogen are surrounded by a luminous zone. It is believed that the light comes from solid particles of the sodium amalgam carried up by the gas. *W. D. B.*

Triboluminescence of potassium sulphate. *D. Gernez. Comptes rendus*, 140, *1234* (*1905*).—Potassium sulphate does not emit light when crystallizing but only when the crystals are crushed or rubbed. It is not necessary that other substances shall be present in solution or that the potassium sulphate shall be fused before being recrystallized. *W. D. B.*

Crystallography, Capillarity and Viscosity

The diamagnetism of bismuth. *A. Leduc. Comptes rendus*, 140, *1022* (*1905*).—Molten bismuth was allowed to solidify in spherical glass vessels while in an intense magnetic field. The crystallization took place in such a way as to make the direction of maximum permeability the same as that of the magnetic field. *W. D. B.*

On isodimorphism. *F. Wallerant. Comptes rendus*, 140, *447* (*1905*).—When rubidium nitrate is added to a solution saturated with respect to potassium nitrate, the series of solid solutions with potassium nitrate in excess has the axes varying continuously with increasing amount of rubidium nitrate. *W. D. B.*

Experimental determination of the surface-tension and the molecular weight of liquid nitrous oxide. *L. Grunmach. Drude's Ann.*, 15, *401* (*1904*).—The method of capillary waves was used which the author has previously shown is well adapted for determining surface-tension and molecular weight of liquid gases. The value of the surface-tension of nitrous oxide comes 26,323 dynes per cm while the molecular weight is found to be 43.52, agreeing very well with the determinations in the gaseous state, *i. e.*, 44.08. *H. T. B.*

Thickness and tension of the capillary film. *G. Bakker. Zeit. phys. Chem.*, 51, *344* (*1905*).—Reinold and Rücker found thicknesses of 5-25$\mu\mu$ for a soap bubble film at ordinary temperatures. The author calculates a negative pressure of 150 Atm. when the film becomes black. *W. D. B.*

Attraction observed between liquid drops suspended in a liquid of the same density. *V. Crémieu. Comptes rendus*, 140, *80* (*1905*).—If a drop of olive oil be allowed to rise through aqueous alcohol of very nearly the same density, the drop will rise vertically. If two or more drops be allowed to rise simultaneously, their paths will converge somewhat. *W. D. B.*

The cause of solid films of peptone on a water surface. *M. V. Metcalf. Zeit. phys. Chem.*, 52, *1* (*1905*).—If a drop of peptone solution be allowed to fall into water, a solid film is formed on the surface of the water. The film spread over a moistened glass surface but not over a dry one. The most probable explanation of the phenomenon is that surface tension effects bring about a chemical reaction at the surface, one of the products being very insoluble in water. *W. D. B.*

On the toughness and rigidity of surface of liquids and liquid films. *K. Schutt. Drude's Ann.*, 13, *712* (*1904*).—Coulomb's method was used to study the surface effects with good results. A retarding action was not observed in the case of sulphuric acid on account of the absorption probably of moisture from the air. Water, sodium carbonate, alcohol, and mercury are among the substances studied. *H. T. B.*

The hydrates of acetol. *A. Kling. Comptes rendus*, 140, *1040* (*1905*).—Viscosity determinations on solutions of acetol in water lead the author to believe in the existence of hydrates containing one, two, four and eleven of water. *W. D. B.*

The viscosity of liquid mixtures. II. *A. E. Dunstan. Zeit. phys. Chem.*, 51, *732* (*1905*).—Reviewed (9, 440) from *Jour. Chem. Soc.*, 87, *11* (*1905*).

On the dependence of the viscosity of nitrogen on the temperature. *A. Bestelmeyer. Drude's Ann.*, 13, *944* (*1904*).—The method of measurement adopted was that of the flow through capillary tubes. A formula deduced by Sutherland is shown to be in agreement with previous results of Holman and Barus over a range from 0° to 300°. The relationship is tested in the present work over a range from —190° to 300°. The paper is a very complete one and the work is carefully carried out. *H. T. B.*

On the cooling observed in the bending of steel bars. *A. Wassmuth. Drude's Ann.*, 13, *182* (*1904*).—A comparison of theory with results for the cooling effect at different temperatures produced in steel bars by bending. The author deduces the temperature coefficient of the modulus of elasticity. A thermo-couple of iron and constantan was used to obtain the small temperature changes. *H. T. B.*

Do crystals soften near the melting-point? *N. Slatowatsky and G. Tammann. Zeit. phys. Chem.*, 53, *341* (*1905*).—Experiments were made on the plasticity of naphthalene at temperatures below the melting point. There were difficulties owing to the presence of air bubbles and of slight impurities in the naphthalene. As these were eliminated, the range over which naphthalene softened became less, but the authors are not prepared to give a final answer to the question which forms the title of the paper. *W. D. B.*

ERRATA

In Mr. Bray's article, 7, 92 (1903), the following changes are to be made:
p. 98, line 11, 100 k_1 instead of k_1.
p. 99, line 1, Exp. 4, 326 instead of 62.
p. 100, line 4, Exp. 8, 18.8 instead of 16.8.

p. 102, line 2, Exp. 12, 59 instead of 50.
p. 102, line 2 from bottom, insert "overnight" after "standing."
p. 106, footnote, K_2O instead of K_2.
pp. 108, 113, Exp. 34, 0.097 instead of 0.091.
p. 110, line 6, less instead of more.
p. 112, line 1, $D + \frac{1}{6}x$ instead of $\rho + \frac{1}{6}x$.
p. 112, line 7, 34 instead of 35.
p. 112, line 8, (D—10.01); *i. e.* by differentiation 0.01 $\frac{\Delta R}{\Delta D}$ instead of (B—1); *i. e.* $\frac{\Delta R}{\Delta B}$.
p. 113, Exp. 13, 0.19 instead of 0.019.
p. 113, Exp. 24, 3.85 and 0.197 instead of 2.85 and 0.094.
p. 117, line 18, 7.3 instead of 8.6.

EQUILIBRIA IN SILVER CHLORIDE SOLUTIONS

BY ROGER CLARK WELLS

In the most satisfactory method known for determining the combining proportions between silver nitrate and metallic halides, it is required to bring the solution of silver halide to a point where it yields equally intense opalescent precipitates with excesses of ionized silver and halide.[1] In practice, one can rarely attain this point at the first trial and it is then desirable to estimate from an observed ratio of the two opalescences just how much silver or chloride, as the case may be, will be necessary to attain the desired point. During work upon the atomic weight of sodium, these quantities were calculated for silver chloride by applying the mass law, from its solubility as measured by the nephelometer, but in practice the calculated amounts were usually too great. Since that work was finished it has seemed worth while to me to try to discover the cause of this slight discrepancy, and especially to find out whether the mass law can be applied quantitatively in this case. With this end in view I first studied the methods of nephelometry in considerable detail. The results obtained, described in a separate paper,[2] were very helpful in studying this problem. The present paper, therefore, records experiments concerning the application of the mass law to solutions of silver chloride.

Much has been written concerning the applicability of the mass law (or concentration law) to ionic concentrations. As is well known, Ostwald's "dilution law" finds experimental fulfilment with "weak electrolytes" but fails with "strong electrolytes" for which various empirical equations have been stated by Rudolphi, van't Hoff and others. Now it has been shown thermodynamically that the mass law could only be expected to hold in solutions where the ions could be assumed to be beyond the spheres of influence of the molecules and of each other.

[1] Stas: Oeuvres complètes, 1, 755. Richards and Wells: Jour. Am. Chem. Soc., 27, 459; Zeit. anorg. Chem., 46, 56 (1905).

[2] Wells: Am. Chem. Jour., 35, 99 (1906).

Most experiments made to test the dilution law, however, are concerned with relatively concentrated solutions. For example, with KCl we have:

V liters	a	$K = \frac{a^2}{(1-a)v}$
10	0.873	0.60
20	0.903	0.41
100	0.956	0.21
500	0.989	0.18
1000	0.994	0.16

At dilutions over 500 liters the variation of "the constant" becomes less and less. The method of conductivity ceases to be of use for the investigation of greater dilutions because of the small change of a. In order to study ionic-concentration relations at greater dilutions, one must resort to solubility experiments with slightly soluble salts, in which the ionic concentrations are varied by the addition of "a common ion" instead of by dilution. For this case there are the two well-known solubility principles.[1]

1. In a saturated solution of a partly ionized substance, the concentration of the un-ionized part remains constant.

2. The solubility-product, *i. e.*, the product of the ionic concentrations, is also a constant.

As regards the first principle, it can only be said that one would expect it to be true for dilute solutions. No direct proof of it has ever been given because only total solubilities can be determined directly, and the true measure of the degree of dissociation is still a disputed matter. Goodwin, assuming electromotive force to be a good measure of the ionic concentrations, shows verification of the principle.[2]

The second principle is more directly the application of the mass law to ionic concentrations. This also has never been put to a direct experimental test unless in connection with the first principle. For verification of the two principles together, many

[1] Noyes: Zeit. phys. Chem., 6, 242 (1890).
[2] Goodwin: Ibid., 13, 608 (1894).

experiments upon solubility and electromotive force may be mentioned.[1] After a careful study of these experiments one must admit that they all possess a common defect, namely, the ionic concentrations are calculated in a circuitous fashion instead of being measured directly. Usually they are calculated from conductivity measurements. Noyes got a fairly good verification of the solubility principles in some cases, *e. g.*, with silver bromate. On account of small deviations between theory and observation, however, he later reversed the process, assuming the solubility principles in order to calculate the dissociations from solubility measurements. Goodwin made different assumptions to calculate the dissociations, sometimes employing electromotive force measurements. His results do not enable one to point out directly the constancy of the solubility-product, but agreement of calculated and observed electromotive forces would tend to indicate such a constancy. He found that the observed and calculated values agree with moderately soluble salts only when the solubility is not depressed too much by a common ion, *i. e.*, the solubility-product appears to wander from constancy as the ionic concentrations diverge widely. With very insoluble depolarizers the theory of a constant solubility-product finds very good verification even with extremely wide variation of the ionic concentrations. Goodwin, therefore, concludes that the "solubility-product" of a very insoluble salt is constant and that the concentration of the undissociated molecules is also constant. Hence from the work of both Noyes and Goodwin the mass law appears to be applicable to the ions of a very insoluble salt in solution.

I do not claim that the following experiments prove the solubility principles more conclusively than the best of former experiments, but they attack the matter in a new and direct fashion and in a way well suited to illustrate the principles to students of analytical chemistry.

Silver chloride was chosen as the insoluble salt because the concentrations of its ions in solution could be measured with the

[1] Nernst: Zeit. phys. Chem., 4, 381 (1889). Noyes: Ibid., 6, 241 (1890); 9, 610 (1892). Goodwin: Ibid., 13, 577 (1894).

nephelometer.[1] The results thus attainable are accurate to a few percent for concentrations varying between about 0.0001 and 0.000001 normal, as has been well proven by many experiments. Silver chloride may be considered a strong electrolyte. The equilibria under consideration are as follows:

Solid		Silver chloride		Ionized		Ionized
silver chloride	⇐	in solution	⇐	silver		chlorine

It should be observed that the ionized chlorine is, in general, made up partly of ionized silver chloride and partly of ionized alkali chloride; the case of ionized silver is similar.

When silver chloride is precipitated (by mixing silver nitrate and potassic chloride) there is also in the solution molecular potassium nitrate and its ions. For nephelometric purposes this is highly advantageous. The equilibria were, therefore, studied in its presence. Furthermore, to prevent every possibility of hydrolysis a very small known amount of nitric acid was allowed to be present. Four solutions were prepared in identical fashion, but they varied in concentration from an extremely small excess of $AgNO_3$ in one, through the middle point to a similarly small excess of KCl in the last. They were made by precipitating 0.05 N $AgNO_3$ with 0.05 N KCl. Dilute solutions were used to prevent occlusion. There thus resulted solutions of the following concentrations:

0.025 N KNO_3
0.000012 N AgCl approximately
0.000016 N HNO_3.

Certain gases dissolved from the air were probably present in concentrations just about equal to the silver chloride. The HNO_3 would also aid in producing constant conditions in their presence. These solutions were agitated in contact with the precipitates, tested occasionally in the nephelometer and finally brought to the concentrations desired and to the temperature of 23° C. When the measurements began, two solutions had had over two weeks in which to attain equilibrium and two others over a month.

[1] Richards and Wells: Am. Chem. Jour., 31, 235 (1904).

The nephelometric methods will now be described in some detail as they have not been given elsewhere when standard glasses have been used. Precipitation of actual silver chloride solutions by an excess of a common ion will serve, practically, to completely precipitate the other ion from solution. The molecular remnant (or the ionic remnant) not precipitated amounts to only about 0.0000002 gram-equivalent per liter.[1] Hence very small ionic concentrations can be determined in this way. Instead of producing known opalescences for comparison at every measurement, the method was adopted of standardizing three glasses in the first place, and then comparing unknown opalescent precipitates with the standard glasses. By thus reducing the number of variables, irregular deviations could more readily be accounted for. The standardization of the ground glasses will next be described.

All the precautions mentioned in a previous paper upon nephelometric measurements were observed in these measurements.[2] The glasses selected for standardization were of such intensities as corresponded to the opalescences which it was designed to measure. They were placed in the nephelometer so that the light always fell upon them at the same angle. The position selected was the smooth top of a "sliding jacket," the jacket being always perpendicular to the horizontal rays of light. The standard opalescences were precipitated from solutions made by diluting 0.001 N solutions of $AgNO_3$ and KCl. Let y represent the number of cubic centimeters taken, and suppose it diluted to 29 cc, the volume of each nephelometer-tube solution after its precipitation. The normality of the opalescence would then be

$$\frac{N}{1000} \times \frac{y}{29}$$

and if this expression be multiplied by r_0, the reading of exposed column in mm, it gives the normality of the opalescence of which 1 mm exposed column would be equivalent to the standard glass.

$$\text{Standard glass} = \frac{N}{1000} \times \frac{y}{29} \times r_0.$$

[1] Richards and Wells: Jour. Am. Chem. Soc., 27, 459 (1905).
[2] Wells: Am. Chem. Jour., 35, 99 (1906).

The concentrations in terms of normal are very small for AgCl solutions. I therefore propose the term "micro-equivalent," a millionth part of an equivalent. That amount in a liter would be a "micro-normal" solution. Hereafter all concentrations will be so expressed. That usage has all the advantages in calculation and thought which the conception normal possesses and saves the notation with many ciphers or powers of ten.

The glasses were standardized by reference to precipitates produced from known chloride as well as from known silver solutions. Below, a_s represents the values referred to chloride precipitated by an excess of $AgNO_3$; b_s the values of the glasses compared to precipitates from silver solutions with excess of KCl. These opalescences were produced with various electrolytes present, mostly HNO_3 and KNO_3, precipitated by a proper excess and recorded at their time of maximum opalescence. The numbers represent micro-equivalents per liter required to produce a column 1 mm. long equivalent to standard glass. Each number corresponds to a separate precipitate.

GLASS 1 (intense)

a_s	b_s
1510	1280
1460	1620
1510	1270
1110	1190
1160	1190
1470	1450
1250	1530
Mean 1350	1360

Mean of a_s and b_s 1360

GLASS 6 (medium intensity)

a_s	b_s
280	340
240	380
310	360
280	280
230	250
240	250
320	
Mean 271	Mean 310

Mean of a_s and b_s 290

GLASS 3 (weak)

a_3	b_3
121	—
117	156
137	134
200	186
170	132
170	156
148	150
138	—
170	—
158	Mean 152
126	
146	
—	
Mean 150	

Mean of a_3 and b_3 151

After the glasses had been standardized, any unknown concentration of either silver or chlorine could be very quickly determined.

When an ionic concentration in one of the four solutions was to be measured, a pipette full of the solution was placed in a nephelometer tube and precipitated by a proper excess of the opposite ion. The opalescence so produced was compared with a standard glass, and the reading, r, recorded when the opalescence was at a maximum. From the previous equation, the value of the standard glass divided by r gives at once the micro-normality of the unknown opalescence. The change in concentration produced by the precipitant was negligible in most cases.

Below are given the results of measurements of the four AgCl solutions. They fall into two sets, A and B. Series A was obtained first. The solutions were next used for making certain electromotive force measurements to be described shortly. During their employment for this purpose, they were shaken frequently and occasionally unstoppered. They were as usual maintained at 23° ±2 and in the dark. Afterwards further nephelometric measurements, Series B, were taken. No change had occurred in the ionized silver concentrations, but some unaccountable change had occurred in the chlorine concentrations. I am at a loss to account for this change. Nevertheless, all deduc-

tions to be made could be made from either series, except as to the absolute usual solubility of AgCl. For my purposes the average of the results are taken, in order to compare the nephelometric with the electromotive force measurements. Each reading records the intensity of a separate opalescent precipitate. Those in Series A were made at widely differing times. All are recorded in the order of observation.

		Micro-equivalents per liter C_{Cl}		Micro-equivalents per liter C_{Ag}		Solubility product
Solution I	A	19				
		15		11		
		17	16	13	12	
		12		13		
		17				
	B	7.3	7	14	14	
		5.9		13		
Mean			12		13	156
Solution II	A	5.0				
		5.6		50		
		6.3		44		
		5.1		36		
		6.1		37		
		5.2	5.8	36	38	
		5.7		37		
		6.8		28		
		7.5		36		
		5.8		39		
		4.5		38		
		6.5				
	B	3.0	3.1	33	36	
		3.1		38		
				37		
				38		
				33		
Mean			4.5		37	166
Solution III	A	57		3.6		
		44		3.8		
		59	53	3.9	3.7	
		52		4.8		
		54		3.7		
				3.0		
				2.9		

		B	29 } 26		5.4 } 4.2	
			22 }		3.9 }	
					3.4 }	
		Mean	40		4.0	160
Solution IV	A		7.2 } 8.6		20 } 23	
			7.5 }		23 }	
			11.4 }		22 }	
			8.3 }			
		B	4.1 } 4.1		25 } 25	
			4.0 }		25 }	
		Mean	6.4		24	154

The four "solubility-products" are 156, 166, 154 and 160, the mean 159. This seems to be an excellent direct verification of the solubility principles, *i. e.*, of the applicability of the mass law to very dilute solutions of "strong electrolytes."

As regards the absolute value of this solubility-product, it represents little because of the unaccountable change in the chlorine concentrations between Series A and B. If Series A alone is considered, it yields a solubility-product 200. If Series B is taken, the value is about 100. The solubility of silver chloride in the usual state of aggregation has been given by other investigators as follows:

Kohlrausch and Rose	18°	1.5 mg. per liter
Böttger	20°	1.5 "
Goodwin	25°	1.8 "
Thiel	25°	2.0 "
Kohlrausch and Rose	26°	2.2 "
" " "	34°	3.0 "

The interpolated mean of all gives about 1.9 mg per liter at 23° and assuming complete ionization, this would give a solubility-product of 177 micro-equivalents per liter. Probably the variation of the solubility with the state of aggregation makes these numbers of little absolute significance.[1] The state of aggregation was probably the same in each of the four flasks in this investigation, however.

[1] Richards and Wells: Zeit. anorg. Chem., 46, 82 (1905).

If the extreme limits in ionic concentrations had been more widely extended, the nephelometer would not have served, for with heavier opalescences than 100 micro-equivalents per liter, premature clotting occurs, and with scantier ones than 1, the excess required to secure complete precipitation begins to dissolve the precipitate. A part of a very scanty precipitate formed from other than AgCl solutions remains in solution to constitute the molecular concentration, whereas in an actual AgCl solution that is already present, hence the standard glasses for very weak opalescences have somewhat too high values, and the small concentrations measured above are also somewhat too great. This source of error may account for the higher constants 166 and 160, where the limits were widely separated.

In view of the reliability of electromotive force as a measure of small concentrations, and as a check upon the nephelometric method, experiments were undertaken with concentration cells, employing the four solutions whose ionic concentrations were known.

A properly prepared piece of silver placed in any of these solutions should constitute a half-electrode which might be measured against any other half-electrode. The simplest arrangement was, of course, to measure them in pairs, thus yielding six possible concentration cells. In theory, such a concentration cell,

Silver	Dilute ionized silver	Concent. ionized silver	Silver

has no peculiarities because the other ion happens to be chloride. Practically, however, such a cell with no solid AgCl present would be very easily polarized on account of the small concentration of silver ions. The latter could be so largely precipitated by a small current as to spoil the concentrations completely. The usual way to overcome this difficulty is to place a layer of the insoluble "depolarizer" AgCl around the metal. This furnishes or takes up silver ions, as the case may be, through the operation of the principle of the constant solubility product.

When the concentration of the chloride ion is large compared to that of silver, it suffers relatively little change, and thereby generates a more constant ionic silver cencentration. The efficacy of depolarizers is witnessed by their use in all standard cells. Experiments showed that here also a depolarizer was necessary to secure good results.

At first considerable time was spent in preparing constant silver electrodes. Pieces of silver beaten flat and plated in potassium silver cyanide often differed by some millivolts among themselves, and the inconstancy remained for the most part when they were chlorinated electrolytically. Uniformly drawn wires, plated and chlorinated as recommended by Goodwin[1] did not differ among themselves, but unfortunately they showed very decided polarization effects in the sense that silver ions could be very quickly precipitated from the solutions, but only slowly produced, *i. e.*, AgCl seemed to dissolve to saturation rather slowly. Finally, however, electrodes were obtained which were both constant and not easily polarizable. On platinum wires, sealed into glass tubes, were fused pieces of platinum foil 1 x 2 cm. These were plated by a current of about 0.05 ampere for about 30 minutes, and then short-circuited in the same solution until they showed less than 0.1 millivolt against each other. They were then thinly chlorinated and after a few washings in pure water, allowed to rest in the saturated AgCl solutions under investigation, in the little tubes usually employed as "half-electrodes."

The electromotive forces were measured by the usual Poggendorf compensation method, with a very sensitive D'Arsonval galvanometer of high resistance as indicating instrument. With a potential gradient of 0.001 volt per 10 ohms (on an Ostwald potentiometer box) the tenths of a millivolt could be obtained by interpolation from the galvanometer swings. The potential gradient was standardized by reference to a cadmium cell whose electromotive force was taken as 1.019 volts at 23°.

The four tubes from the half-electrodes dipped into a single

[1] Zeit. phys. Chem., 13, 597 (1894).

connecting solution. This was rather concentrated KNO_3 in the final measurements. Fortieth normal KNO_3 was tried but offered more resistance. Concentrated KCl was also tried. No difference in electromotive force could be detected as a result of these changes. Other investigators have shown that a concentrated connecting solution or the presence of a neutral salt like KNO_3 in each of the half-electrodes drowns out the production of potential at the liquid junctions. For both reasons, therefore, the theoretical calculation becomes somewhat simplified, for the transport numbers do not enter the formulas. The formula reduces to:

$$E = RT \ln \frac{c_1}{c_2}.$$

At 23° this becomes:

$$E = 0.0587 \log_{10} \frac{c_1}{c_2}$$

where c_1 = concentration of concentrated silver solution
" c_2 = " " dilute " "

Since E varies as log c_1 and c_2 one might expect in advance that the nephelometric values would be sufficiently accurate. The only assumption made in deriving the formula is that the solution tension is independent of the nature of the solution. E is also calculated below by the same formula, using the known chloride instead of the silver concentrations. During the preliminary observations, the solutions bathing the electrodes were frequently exchanged for fresh solution in order that the AgCl layer upon the electrode might come to equilibrium with the solution and all accidental concentration polarization be removed.

The agreement of observed and calculated values is very satisfactory, whichever method of calculation is employed.

If one considers the first method of calculation, these measurements differ from any heretofore made, to the best of my knowledge, in that the metallic concentrations were very small and were determined directly. To determine these concentrations no solubility had to be known nor were hardly any assumptions necessary. Further, no estimated correction for the extent

OBSERVED E. M. F.

Combination of solutions	II–III	II–IV	II–I	IV–III	IV–I	I–III
Preliminary observation, electrodes attaining equilibrium	0.0481	0.0095	0.0210	—	0.0130	0.027
	0.0483	0.0100	0.0220	0.0390	0.0124	0.026
	0.0478	0.0105	0.0225	0.0381	0.0120	0.026
	0.0500	0.0098	0.0250	0.0390	0.0050	0.0272
	0.0491	—	0.0262	0.0390	—	0.0275
	0.0520	—	—	0.0315	—	0.0278
	0.0540	—	—	0.0436	—	—
Final values ($t = 23°$)	0.0560	0.0100	—	—	0.0165	—
	0.0558	0.0101	0.0241	0.0452	0.0139	0.0312
	0.0565	0.0104	0.0250	0.0457	0.0143	0.0305
	0.0550	0.0102	0.0245	0.0456	0.0147	0.0310
Mean of final values	0.0559	0.0101	0.0245	0.0455	0.0149	0.0309

CALCULATED E. M. F.

Ratio of silver concentrations	9.24	1.54	2.84	6.00	1.845	3.25
E. M. F.	0.0561	0.0110	0.0266	0.0457	0.0156	0.0300
Ratio of chloride concentrations	8.88	1.42	2.47	6.25	1.877	3.33
E. M. F.	0.0557	0.0090	0.0230	0.0467	0.0161	0.0306
Mean of two methods of calculation	0.0559	0.0100	0.0248	0.0462	0.0158	0.0303

of ionization was required. The results are, therefore, a direct proof of the applicability of Nernst's formulae for electromotive force and strengthen the conception of solution tension, showing, at least, the constancy of the latter within certain limits.

If the second method of calculation is considered, one can easily see that it reduces to the first method when the principle of the constant solubility-product is assumed, for then

$$\frac{c_1(\mathrm{Ag})}{c_2(\mathrm{Ag})} = \frac{c_2(\mathrm{Cl})}{c_1(\mathrm{Cl})}.$$

There is thus no difference in theory between an electrode of the first class and one of the second class, although the latter succeed in avoiding polarization. The agreement by the second

method of calculation, therefore, verifies the solubility principles in a new way, as Goodwin has already pointed out.[1] These measurements differ from Goodwin's in the directness of the determination of the anion concentrations, and they involve no correction for the extent of dissociation. As a matter of fact, Goodwin secured agreement between observation and calculation when the concentration of the common ion was sufficiently small.

The results both for calculation as electrodes of the first class and as of the second class are somewhat better than those obtained by Nernst, using more concentrated solutions and correcting for incomplete dissociation.[2]

Lastly, the electromotive force measurements show very conclusively that the nephelometric methods used in this and former work are trustworthy.

I take this opportunity of expressing my sincere thanks to Mr. W. D. Hutchinson, of Oxford University, for assisting me in the preparation of solutions and in some of the preliminary observations. Most of the results were obtained at Harvard University, but some final observations were made at the University of Pennsylvania.

Summary

The general conclusion to be drawn from these experiments is that AgCl (of a definite state of aggregation) has a constant solubility-product; more broadly, the mass law like many other physico-chemical laws approaches exact fulfilment at great dilutions, even when applied to ionic concentrations of "strong electrolytes."

University of Pennsylvania,
December, 1905

[1] Zeit. phys. Chem., 13, 622 (1894).
[2] Ibid., 4, 161 (1889).

THE ALLOYS OF ANTIMONY AND TIN

F. E. GALLAGHER

Some years ago Reinders[1] made a careful study of the freezing-points of the alloys of antimony and tin. This work was supplemented by a microscopical examination of selected samples. The diagram, as worked out by Reinders, is given in Fig. 1. There are four branches to the freezing-point curve

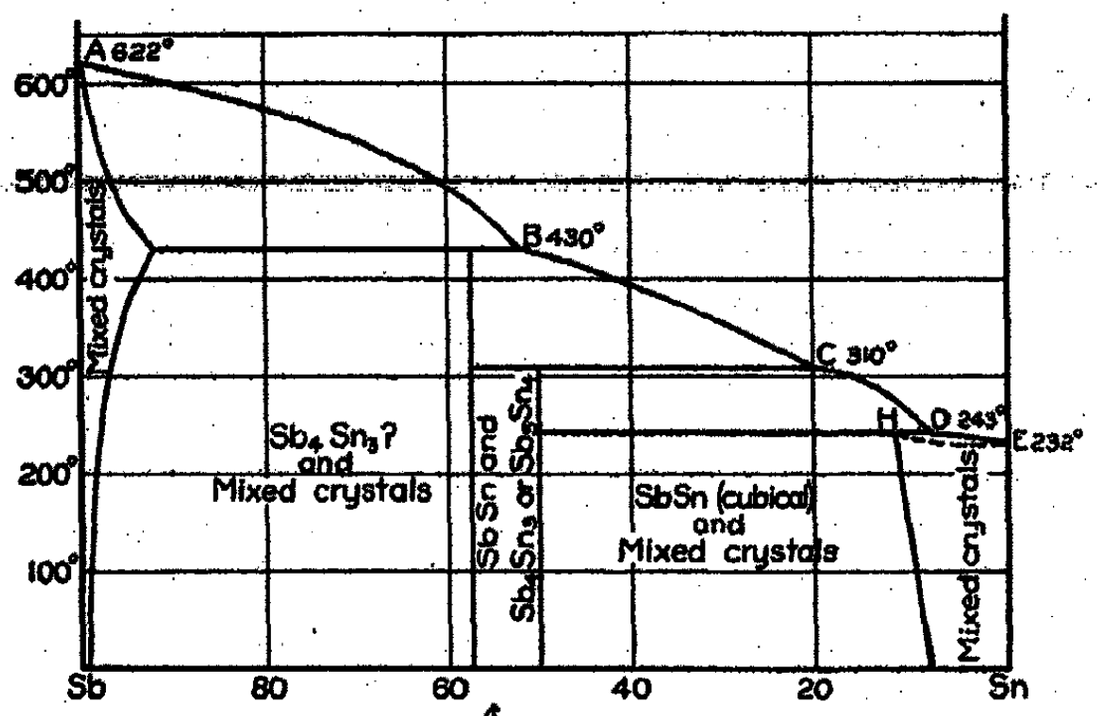


Fig. 1

and no eutectic, the first addition of antimony raising the freezing-point of the tin. Along the first branch AB, we have a solid solution; along the second branch BC the compound Sb_4Sn_3 was said to crystallize though Reinders was willing to admit the possibility of the compound being really Sb_3Sn_4. The compound SbSn was said to be the solid phase along CD while van Bijlert[2] had already proved that a solid solution separated at the tin end of the curve.

Chiefly owing to the uncertainty with regard to the alleged compound Sb_4Sn_3, it was deemed advisable to make a careful microscopical examination of the antimony-tin alloys. The

[1] Zeit. anorg. Chem., 25, 113 (1900).

[2] Zeit. phys. Chem., 8, 843 (1891).

freezing-point curve given by Reinders seems to have been determined carefully and I have not checked it systematically except where it did not accord with the facts furnished by the microscopical examination.

It was soon found that there are no compounds between antimony and tin, the four solid phases being four sets of solid solutions. These will be called the α, β, γ and δ crystals, beginning at the high melting or antimony end of the freezing-point curve as suggested by Heycock and Neville. The final diagram is given in Fig. 2. The field for the α-crystals

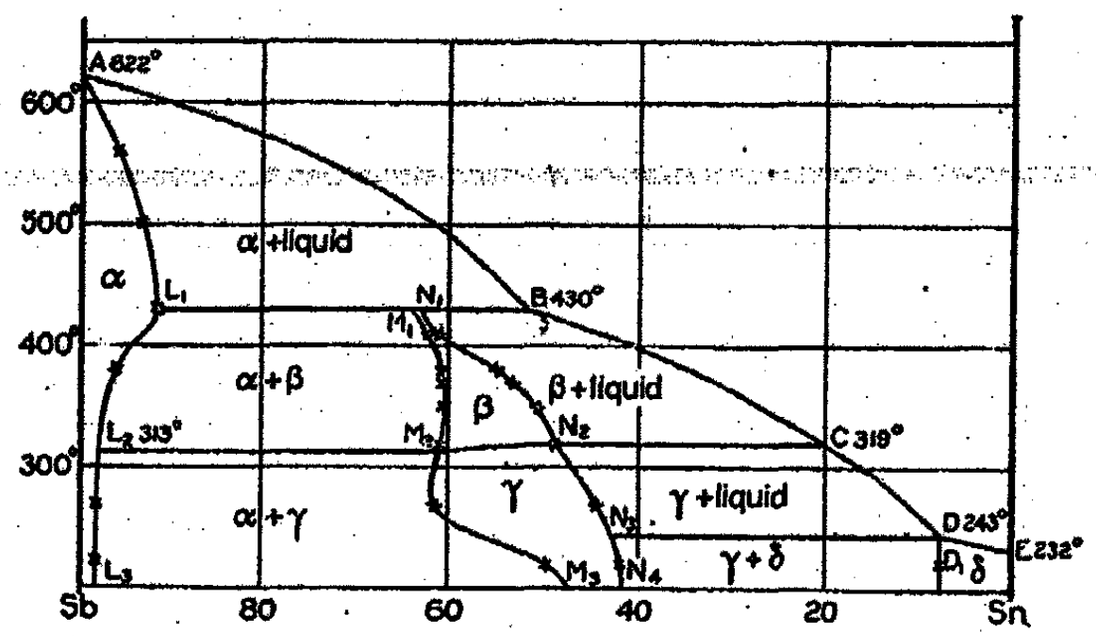


Fig. 2

lies to the left of $AL_1L_2L_3$. Pure β-crystals occur in the field $M_1M_2N_2N_1$. In the presence of the α-crystals the β-crystals break down at 313°, while they break down at 319° in presence of the melt. Pure γ-crystals are to be found in the field $M_2M_3N_3N_2$ while pure δ occurs in the field EDD_1. Theoretically there is a field for δ and liquid just below ED but the melt solidifies so nearly without change that it was impossible to detect two points even pyrometrically. The solidus is, therefore, $AL_1M_1N_1N_2N_3DE$.

The line L_2M_2 does not occur at all in the Reinders diagram and the line N_2C was found by Reinders at 310° instead of at 319°. In my work these lines were determined both by heating curves and by cooling curves. Although the breaks were slight,

they were determined many times with a temperature variation of but one degree. Four hundred grams of alloy were taken and the heating or cooling was done in an electric furnace with a temperature change of 3/4° to 2° per minute. The temperature was measured by means of two Pt, Pt–Ir thermocouples arranged in series. The large mass of the alloy, the control of the heating and cooling rates, and the double couples all aided in making possible a close determination of the temperature.

Since the determinations of the 430° inversion-point B and the 243° inversion-point D agreed very closely with the corresponding values obtained by Reinders, it was deemed desirable to discover the cause of the discrepancy of 9° in the 319° inversion-point, C. It was found that the rate of cooling had a marked influence on the result. When the alloy cooled at the rate of three degrees per minute the break was carried down to 312°, seven degrees below the value obtained with a slower rate of cooling. Since Reinders had a cooling rate of four degrees per minute, it is not surprising that he should have obtained some results as low as 305°. The only way to be certain that the rate of heating or cooling is introducing no errors is to determine both heating and cooling curves.

In Fig. 1 the maximum concentration of the δ crystals is given as 11 percent Sb while in Fig. 2 the limiting line for these crystals starts from D at 8 percent Sb. Reinders obtained the value of 11 percent Sb by extrapolation from v. Bijlert's results. It is always dangerous to extrapolate and the matter is made worse in this case by the fact that v. Bijlert was working with a ternary alloy of antimony, tin and silver instead of with the binary alloy of antimony and tin. The microscopical examination does not justify this extrapolation. In the chill-cast specimens the second phase, small cubical crystals of γ, first appear at 8 percent Sb. After annealing for eight weeks in boiling naphthalene (218°), the γ-crystals are still present though they are no longer cubical, their edges being rounded off.

From a high-grade antimony and Banca tin 99.9 percent pure, sixty-three castings were made, containing the following percentages of antimony by weight:

1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 15, 20, 30, 35, 38, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49, 50, 51, 52, 53, 54, 55, 56, 57, 58, 59, 60, 61, 62, 63, 64, 65, 66, 66.6, 67, 68, 69, 70, 75, 80, 85, 87, 89, 91, 92, 93, 94, 95, 96, 97, 98, 99.

A graphite crucible was used and a gas furnace. The antimony was melted first, the flame removed, and the tin added. Since the melting-point of antimony is 622° and that of tin 232°, the tin melted rapidly in the molten antimony, at the same time cooling the melt and thereby decreasing the danger of oxidation. The melts were very clean, *i. e.*, free from oxide, showing that the components did not burn out to a marked extent. The melt was cast into bars in a graphite mould and specimens for annealing and polishing were sawed from the water-chilled bars. Annealings were made at 218°, 270°, 320°, 360° 370°, 380°, 410°, 430°, 500° and 560°. The annealings were continued until equilibrium was found to have been reached, after which the specimens were polished, etched, and examined under the microscope. From observations on the crystal forms and on the changes in homogeneity, the limits of the fields and the nature of the phases were determined. The β- and γ-crystals have the same form and cannot be distinguished satisfactorily under the microscope. The existence of the two forms was shown by the heat effect along the lines $L_2M_2N_2C$. The portion of the solidus curve $N_1N_2N_3$ could be determined sharply by microscopic examination though this is not the case with all alloys. The melt would first appear as a broadening of the lines that marked the crystal edges, and the increase in the melt with changing composition was rapid.

The examination of the chill-castings was important in that it showed how little reliance can be placed on such samples. All the castings between 8 percent and 97 percent Sb were inhomogeneous and the homogeneous fields for the β- and γ-crystals appeared only on annealing.

The lowest points given in the diagram are at 218° and were obtained by annealing in boiling naphthalene. The slowness with which equilibrium is reached at this temperature is shown by the fact that three weeks annealing was not sufficient

and that it was necessary to anneal for five weeks longer. On the first examination the homogeneous γ-crystals had formed, but they were so small that on etching they gave a silvery surface which meant nothing. Upon longer annealing the crystals grew to a larger size, from which the crystal form and the limits of homogeneity could be observed.

Some of the annealings had to be made at temperatures between 243° and 319°. For the constant temperature bath several organic substances were tried, such as β-naphthol, phthalic anhydride, etc., but these were all unsatisfactory and the annealings were finally made in a special form of gas furnace which was held for twenty-two days at a temperature of 270° ± 10°. All annealings above 320° were done in an electric annealing furnace, the temperature of which could be held constant to ± 2°.

As the temperature rises the equilibrium is reached in less and less time. At 320° the heating was continued for eleven hours; at 380° for six hours; at 410° for four hours; at 560° for three hours. When determining the boundaries of the α-field, the specimens were annealed at the desired temperature until successive examinations showed no further change in the specimen. In determining the position of the line M_1M_2, a boundary of the β-field, I held for six hours at 360° specimens which had been annealed at 410° and which were homogeneous at 62 percent Sb and also specimens which had been annealed but three hours at 350° and which were homogeneous only to 57 percent Sb. Both sets of castings gave the same limit of homogeneity, at 60 percent Sb. As this result was obtained starting from either side, it appears certain that equilibrium was reached. During the early part of the work it was believed that a change of crystallization took place at about 66 percent Sb. Longer annealing showed that this was not the case and that the apparent difference was due to the presence of imperfectly formed α-crystals in the castings containing less than 66 percent Sb. It is quite possible that this was caused by the formation of the bulk of the α-crystals as a result of the breaking down of β-crystals. It is to be noticed that the instable extension of the

freezing-point curve CB would pass through a maximum where it met the equally instable extension of the β-field. Judging from the diagram this instable maximum would occur at about 65–66 percent Sb. It is quite possible that this equilibrium was reached temporarily when the molten alloys were chill-cast.

Practically all of the polished surfaces were etched with ferric chloride in alcoholic solution. This worked quickly and gave clear sections. Considerable difficulty was experienced in etching the specimens across the δ solid solution, which is at the tin-rich side. The ordinary reagents blackened the surface so that the structure was marked. The Reinders method of using the specimen as anode in a 1 percent nitric acid solution gave a black coating, which, however, could be removed by the action of a four-volt current through an alkaline solution of concentrated sodium tartrate, the specimen again being made the anode. The bright surface then showed the δ structure.

No experiments have been made below 200° and it would not be justifiable to continue the fields lower until the allotropic forms of tin have been worked out more definitely. Judging from the slowness with which equilibrium was reached at 218°, the working out of fields at still lower temperatures would require an unreasonable amount of time.

The general results of this investigation are as follows:

1. The temperature-concentration diagram for antimony-tin alloys has been determined for temperatures above 200°.

2. Antimony and tin form four series of solid solutions and no compounds.

3. The β-crystals are instable below 313°.

This investigation is one of a series made possible by a grant from the Carnegie Institution. I express my appreciation for the help given me by Mr. B. E. Curry in many of the experimental details, and by Mr. G. B. Upton in the cooling-curve determinations. The work was suggested by Professor Bancroft and has been carried on under his supervision.

Cornell University.

BIBLIOTHÈQUES DE L'UNIVERSITÉ DE PARIS
ORSAY

ON SOLUBILITY CURVES

BY J. E. TREVOR

Writing m_{11} for the mass of the first component in unit mass of the first phase of a two-component system in a two-phase state, the thermodynamic expression for the slope

$$\frac{\partial m_{11}(\theta)}{\partial \theta}$$

of the family of solubility curves

$$m_{11} = m_{11}(p,\theta)$$

with parameter p is well known. It is of interest to establish the corresponding expression for the slope $dm_{11}/d\theta$ of the solubility curve

$$m_{11} = m_{11}(\theta)$$

of a two-component system in a three-phase state—a univariant state.

When the system is in a two-phase state of thermodynamic equilibrium under the pressure p at the temperature θ, the differentials of p, θ, m_{11} are connected by the equation

$$\left(v_2 - v_1 - (m_{21} - m_{11})\frac{\partial v_1}{\partial m_{11}}\right)dp = \left(\eta_2 - \eta_1 - (m_{21} - m_{11})\frac{\partial \eta_1}{\partial m_{11}}\right)d\theta + (m_{21} - m_{11})\frac{\partial^2 h_1}{\partial m_{11}^2}dm_{11}.$$

In this equation, which is due to van der Waals, the letters v_i, η_i, h_i denote the specific volume, the specific entropy, and the specific thermodynamic potential of the i-th phase, and m_{ij} denotes the mass of the j-th component in unit mass of the i-th phase. Now, the appearance of a third phase renders p a function of θ. If the equation remains otherwise unchanged, we shall have

$$\left(v_2 - v_1 - (m_{21} - m_{11})\frac{\partial v_1}{\partial m_{11}}\right)\frac{dp}{d\theta} = \left(\eta_2 - \eta_1 - (m_{21} - m_{11})\frac{\partial \eta_1}{\partial m_{11}}\right) + (m_{21} - m_{11})\frac{\partial^2 h_1}{\partial m_{11}^2}\frac{dm_{11}}{d\theta};$$

or, replacing $dp/d\theta$ by the ratio $\delta H/\delta V$ of the changes of entropy and volume of the system in an isothermal change of the state,

$$(1)\qquad \frac{\partial^2 h_1}{\partial m_{11}^2}\cdot\frac{dm_{11}}{d\theta}=\left(\frac{v_2-v_1}{m_{21}-m_{11}}-\frac{\partial v_1}{\partial m_{11}}\right)\frac{\delta H}{\delta V}-\left(\frac{\eta_2-\eta_1}{m_{21}-m_{11}}-\frac{\partial \eta_1}{\partial m_{11}}\right).$$

The object of this note is to show that the equation (1) is a consequence of the conditions of equilibrium of a two-component system in a three-phase state.

If no constituents other than the two independent components appear in the system, and if we write μ_{ij} for the potential of the j-th component in the i-th phase, the conditions of equilibrium are

$$\mu_{11}=\mu_{21},\quad \mu_{12}=\mu_{22},\qquad \mu_{11}=\mu_{31},\quad \mu_{12}=\mu_{32}.$$

Differentiating these equations within the region of their validity,

$$(2)\quad\begin{cases}\left(\frac{\partial\mu_{11}}{\partial p}-\frac{\partial\mu_{21}}{\partial p}\right)dp+\left(\frac{\partial\mu_{11}}{\partial\theta}-\frac{\partial\mu_{21}}{\partial\theta}\right)d\theta+\frac{\partial\mu_{11}}{\partial m_{11}}dm_{11}-\frac{\partial\mu_{21}}{\partial m_{21}}dm_{21}=0\\ \left(\frac{\partial\mu_{11}}{\partial p}-\frac{\partial\mu_{31}}{\partial p}\right)dp+\left(\frac{\partial\mu_{11}}{\partial\theta}-\frac{\partial\mu_{31}}{\partial\theta}\right)d\theta+\frac{\partial\mu_{11}}{\partial m_{11}}dm_{11}-\frac{\partial\mu_{31}}{\partial m_{31}}dm_{31}=0\\ \left(\frac{\partial\mu_{12}}{\partial p}-\frac{\partial\mu_{22}}{\partial p}\right)dp+\left(\frac{\partial\mu_{12}}{\partial\theta}-\frac{\partial\mu_{22}}{\partial\theta}\right)d\theta+\frac{\partial\mu_{12}}{\partial m_{11}}dm_{11}-\frac{\partial\mu_{22}}{\partial m_{21}}dm_{21}=0\\ \left(\frac{\partial\mu_{12}}{\partial p}-\frac{\partial\mu_{32}}{\partial p}\right)dp+\left(\frac{\partial\mu_{12}}{\partial\theta}-\frac{\partial\mu_{32}}{\partial\theta}\right)d\theta+\frac{\partial\mu_{12}}{\partial m_{11}}dm_{11}-\frac{\partial\mu_{32}}{\partial m_{31}}dm_{31}=0.\end{cases}$$

Let us recall the well-known equations that enable us to express the derivatives of the potentials μ_{ij} by means of the specific extensities of the phases. The equation expressing that the thermodynamic potential

$$H(p,\ \theta,\ M_1,\ M_2)$$

of a given phase of the phase system in homogeneous and of the first degree in the masses M_1, M_2 of the independently variable components of the phase is

$$H=(M_1+M_2).\,h\,(p,\ \theta,\ m_1).$$

Here m_1 is the mass of the first component in unit mass of the phase. From this formulation we find, for the potentials,

$$\mu_1 = \frac{\partial H}{\partial M_1} = h + (M_1 + M_2)\frac{\partial h}{\partial m_1}\frac{\partial m_1}{\partial M_1},$$

$$\mu_2 = \frac{\partial H}{\partial M_2} = h + (M_1 + M_2)\frac{\partial h}{\partial m_1}\frac{\partial m_1}{\partial M_2};$$

or, since $m_1 = M_1/(M_1 + M_2)$,

$$\mu_1 = h + (1 - m_1)\frac{\partial h}{\partial m_1}$$

$$\mu_2 = h - m_1\frac{\partial h}{\partial m_1}.$$

Forming the derivatives of these potentials, noting that

$$\frac{\partial h}{\partial p} = v, \qquad \frac{\partial h}{\partial \theta} = -\eta,$$

and adding to each extensive quantity a subscript i to distinguish the phase, we get the equations in question:

$\frac{\partial \mu_{i_1}}{\partial p} = + v_i + (1 - m_{i_1})\frac{\partial v_i}{\partial m_{i_1}}$	$\frac{\partial \mu_{i_2}}{\partial p} = + v_i - m_{i_1}\frac{\partial v_i}{\partial m_{i_1}}$
$\frac{\partial \mu_{i_1}}{\partial \theta} = - \eta_i - (1 - m_{i_1})\frac{\partial \eta_i}{\partial m_{i_1}}$	$\frac{\partial \mu_{i_2}}{\partial \theta} = - \eta_i + m_{i_1}\frac{\partial \eta_i}{\partial m_{i_1}}$
$\frac{\partial \mu_{i_1}}{\partial m_{i_1}} = + (1 - m_{i_1})\frac{\partial^2 h_i}{\partial m_{i_1}^2}$	$\frac{\partial \mu_{i_2}}{\partial m_{i_1}} = - m_{i_1}\frac{\partial^2 h_i}{\partial m_{i_1}^2}.$

Eliminating the derivatives of μ_{ij} between (2) and these equations, and combining the four resulting equations by eliminating between them the three quantities

$$dp, \qquad \frac{\partial^2 h_2}{\partial m_{21}^2}dm_{21}, \qquad \frac{\partial^2 h_1}{\partial m_{21}^2}dm_{21},$$

we obtain the equation connecting the differentials of m_{11} and θ,

$$\text{D.}\frac{\partial^2 h_1}{\partial m_{11}^2}dm_{11} = \Delta . d\theta; \tag{3}$$

where

$$D=\begin{vmatrix} 1-m_{11}, & \left(v_1+(1-m_{11}\frac{\partial v_1}{\partial m_{11}}\right)-\left(v_2+(1-m_{21})\frac{\partial v_2}{\partial m_{21}}\right), & -1+m_{21}, & 0 \\ 1-m_{11}, & \left(v_1+(1-m_{11}\frac{\partial v_1}{\partial m_{11}}\right)-\left(v_3+(1-m_{31})\frac{\partial v_3}{\partial m_{31}}\right), & 0, & -1+m_{31} \\ -m_{11}, & \left(v_1-m_{11}\frac{\partial v_1}{\partial m_{11}}\right)- & \left(v_2-m_{21}\frac{\partial v_2}{\partial m_{21}}\right), & m_{21}, \quad 0 \\ -m_{11}, & \left(v_1-m_{11}\frac{\partial v_1}{\partial m_{11}}\right)- & \left(v_3-m_{31}\frac{\partial v_3}{\partial m_{31}}\right), & 0, \quad m_{31} \end{vmatrix},$$

$$\Delta=\begin{vmatrix} \left(\eta_1+(1-m_{11})\frac{\partial \eta_1}{\partial m_{11}}\right)-\left(\eta_2+(1-m_{21})\frac{\partial \eta_2}{\partial m_{21}}\right), & \ldots \\ \left(\eta_1+(1-m_{11})\frac{\partial \eta_1}{\partial m_{11}}\right)-\left(\eta_3+(1-m_{31})\frac{\partial \eta_3}{\partial m_{31}}\right), & \ldots \\ \left(\eta_1-m_{11}\frac{\partial \eta_1}{\partial m_{11}}\right)- & \left(\eta_2-m_{21}\frac{\partial \eta_2}{\partial m_{21}}\right), \quad \ldots \\ \left(\eta_1-m_{11}\frac{\partial \eta_1}{\partial m_{11}}\right)- & \left(\eta_3-m_{31}\frac{\partial \eta_3}{\partial m_{31}}\right), \quad \ldots \end{vmatrix},$$

the last three columns of the second determinant being identical with those of the first.

The determinant D is of the form

$$D=\begin{vmatrix} 1-m_{11} & a_1-a_2+x & -1+m_{21} & 0 \\ 1-m_{11} & a_1-a_3+y & 0 & -1+m_{31} \\ -m_{11} & a_1-a_2 & m_{21} & 0 \\ -m_{11} & a_1-a_3 & 0 & m_{31} \end{vmatrix},$$

where

$$a_i=v_i-m_{i1}\frac{\partial v_i}{\partial m_{i1}}$$

$$x=\frac{\partial v_i}{\partial m_{11}}-\frac{\partial v_2}{\partial m_{21}}$$

$$y=\frac{\partial v_1}{\partial m_{11}}-\frac{\partial v_3}{\partial m_{31}}.$$

Expanding D,

$$D=(m_{21}-m_{31})\,a_1+(m_{31}-m_{11})\,a_2+(m_{11}-m_{21})\,a_3 + m_{11}.m_{21}.x+m_{31}.m_{31}\,(y-x)-m_{31}.m_{11}.y.$$

Replacing a_i, x, y by their values, and collecting the coefficients of the v_i and their derivatives, we find

$$D = (m_{11} - m_{31})v_1 + (m_{31} - m_{11})v_2 + (m_{11} - m_{21})v_3$$

$$(4) \qquad = \begin{vmatrix} v_1 & v_2 & v_3 \\ m_{11} & m_{21} & m_{31} \\ 1 & 1 & 1 \end{vmatrix}.$$

The determinant Δ is of the form

$$\Delta = \begin{vmatrix} b_1 - b_2 + u & a_1 - a_2 + x & -1 + m_{21} & 0 \\ b_1 - b_3 + v & a_1 - a_3 + y & 0 & -1 + m_{31} \\ b_1 - b_2 & a_1 - a_2 & m_{31} & 0 \\ b_1 - b_3 & a_1 - a_3 & 0 & m_{31} \end{vmatrix},$$

where

$$b_i = \eta_i - m_{i1}\frac{\partial \eta_i}{\partial m_{i1}}$$

$$u = \frac{\partial \eta_1}{\partial m_{11}} - \frac{\partial \eta_2}{\partial m_{21}}$$

$$v = \frac{\partial \eta_1}{\partial m_{11}} - \frac{\partial \eta_3}{\partial m_{31}}.$$

Expanding Δ,

$$\Delta = \begin{vmatrix} b_1 - b_2 + m_{21}.u & b_1 - b_3 + m_{31}.v \\ a_1 - a_2 + m_{21}.x & a_1 - a_3 + m_{31}.y \end{vmatrix}.$$

Replacing a_i, b_i, u, v, x, y by their values, removing the terms that cancel each other, expanding, and collecting the coefficients of $\partial v_1/\partial m_{11}$ and $\partial \eta_1/\partial m_{11}$, we find

$$(5) \qquad \Delta = -\begin{vmatrix} \eta_1 & \eta_2 & \eta_3 \\ m_{11} & m_{21} & m_{31} \\ 1 & 1 & 1 \end{vmatrix}\frac{\partial v_1}{\partial m_{11}} + \begin{vmatrix} v_1 & v_2 & v_3 \\ m_{11} & m_{21} & m_{31} \\ 1 & 1 & 1 \end{vmatrix}\frac{\partial \eta_1}{\partial m_{11}} - \begin{vmatrix} v_1 & v_2 & v_3 \\ \eta_1 & \eta_2 & \eta_3 \\ 1 & 1 & 1 \end{vmatrix}.$$

The determinants of the third order in the expressions (4), (5) for D, Δ can be expressed with the aid of changes that the

volume V and entropy H of the phase system undergo in a finite isothermal change of state. At constant θ and masses of the independent components of the system, we have

$$v_1\,\delta\mathfrak{M}_1 + v_2\,\delta\mathfrak{M}_2 + v_3\,\delta\mathfrak{M}_3 = \delta V \tag{6}$$

$$\eta_1\,\delta\mathfrak{M}_1 + \eta_2\,\delta\mathfrak{M}_2 + \eta_3\,\delta\mathfrak{M}_3 = \delta H \tag{7}$$

$$m_{11}\,\delta\mathfrak{M}_1 + m_{21}\,\delta\mathfrak{M}_2 + m_{31}\,\delta\mathfrak{M}_3 = 0 \tag{8}$$

$$\delta\mathfrak{M}_1 + \delta\mathfrak{M}_2 + \delta\mathfrak{M}_3 = 0. \tag{9}$$

By elimination of $\delta\mathfrak{M}_1$, $\delta\mathfrak{M}_2$ between (6), (8), (9), between (7), (8), (9), and between (6), (7), (9), we find, namely,

$$\begin{vmatrix} v_1 & v_2 & v_3 \\ m_{11} & m_{21} & m_{31} \\ 1 & 1 & 1 \end{vmatrix} = -(m_{21} - m_{11})\frac{\delta V}{\delta\mathfrak{M}_3}$$

$$\begin{vmatrix} \eta_1 & \eta_2 & \eta_3 \\ m_{11} & m_{21} & m_{31} \\ 1 & 1 & 1 \end{vmatrix} = -(m_{21} - m_{11})\frac{\delta H}{\delta\mathfrak{M}_3}$$

$$\begin{vmatrix} v_1 & v_2 & v_3 \\ \eta_1 & \eta_2 & \eta_3 \\ 1 & 1 & 1 \end{vmatrix} = -(\eta_2 - \eta_1)\frac{\delta V}{\delta\mathfrak{M}_3} + (v_2 - v_1)\frac{\delta H}{\delta\mathfrak{M}_3}.$$

Substituting these values in the equations (4), (5) for D, Δ, we find

$$D = -(m_{21} - m_{11})\frac{\delta V}{\delta\mathfrak{M}_3}$$

$$\Delta = -\left(v_2 - v_1 - (m_{21} - m_{11})\frac{\partial v_1}{\partial m_{11}}\right)\frac{\delta H}{\delta\mathfrak{M}_3} + \left(\eta_2 - \eta_1 - (m_{21} - m_{11})\frac{\partial \eta_1}{\partial m_{11}}\right)\frac{\delta V}{\delta\mathfrak{M}_3}.$$

The equation (3) for $dm_{11}/d\theta$,

$$\frac{\partial^2 h_1}{\partial m_{11}^2}\cdot\frac{dm_{11}}{d\theta} = \frac{\Delta}{D'}$$

hereupon becomes

$$(10)\quad \frac{\partial^2 h_1}{\partial m_{11}^2}\cdot\frac{dm_{11}}{d\theta}=\left(\frac{v_2-v_1}{m_{21}-m_{11}}-\frac{\partial v_1}{\partial m_{11}}\right)\frac{\delta H}{\delta V}-\left(\frac{\eta_2-\eta_1}{m_{21}-m_{11}}-\frac{\partial \eta_1}{\partial m_{11}}\right).$$

This is the equation (1), which is thus seen to be, as asserted, a consequence of the conditions of equilibrium of a two-component system in a three-phase state.

The equation will be expressed a little differently if we eliminate either $\delta\mathfrak{M}_2$, $\delta\mathfrak{M}_3$, or $\delta\mathfrak{M}_1$, $\delta\mathfrak{M}_3$, between equations of the set (6), (7), (8), (9), instead of eliminating $\delta\mathfrak{M}_1$, $\delta\mathfrak{M}_2$. In these successive cases we find

$$(10a)\quad \frac{\partial^2 h_1}{\partial m_{11}^2}\cdot\frac{dm_{11}}{d\theta}=\left(\frac{v_2-v_3}{m_{21}-m_{31}}-\frac{\partial v_1}{\partial m_{11}}\right)\frac{\delta H}{\delta V}-\left(\frac{\eta_2-\eta_3}{m_{21}-m_{31}}-\frac{\partial \eta_1}{\partial m_{11}}\right)$$

$$(10b)\quad =\left(\frac{v_1-v_3}{m_{11}-m_{31}}-\frac{\partial v_1}{\partial m_{11}}\right)\frac{\delta H}{\delta V}-\left(\frac{\eta_1-\eta_3}{m_{11}-m_{31}}-\frac{\partial \eta_1}{\partial m_{11}}\right).$$

The formulations of (10), (10*b*) do not contain quantities characteristic of the third, respectively of the second, phase of the system.

It may here be remarked that equating the second members of the equations (10), (10*a*), (10*b*) may serve as a check on the work. Equating the second members of (10), (10*a*), for example, we find

$$(m_{31}-m_{31})(v_2-v_1)\frac{\delta H}{\delta V}-(m_{21}-m_{31})(\eta_2-\eta_1)$$

$$=(m_{21}-m_{11})(v_2-v_3)\frac{\delta H}{\delta V}-(m_{21}-m_{11})(\eta_2-\eta_3);$$

whence

$$\frac{\delta H}{\delta V}=\frac{\begin{vmatrix}\eta_2-\eta_1 & \eta_2-\eta_3\\ m_{21}-m_{11} & m_{21}-m_{31}\end{vmatrix}}{\begin{vmatrix}v_2-v_1 & v_2-v_3\\ m_{21}-m_{11} & m_{21}-m_{31}\end{vmatrix}}=-\frac{\begin{vmatrix}\eta_1 & \eta_2 & \eta_3\\ m_{11} & m_{21} & m_{31}\\ 1 & 1 & 1\end{vmatrix}}{\begin{vmatrix}v_1 & v_2 & v_3\\ m_{11} & m_{21} & m_{31}\\ 1 & 1 & 1\end{vmatrix}}=\frac{\frac{\delta H}{\delta\mathfrak{M}_3}}{\frac{\delta V}{\delta\mathfrak{M}_3}},$$

the expressions substituted for the determinants of the third order being deduced, as above, from the equations (6), (7), (8),

(9). The equations (10), (10*b*), and the equations (10*a*), (10*b*), can be compared in this same way.

An interesting special case of (10) is the equation for the slope of the solubility curve when only one of the phases has a variable composition. To illustrate, suppose the first component of the system to be an involatile salt, the second component to be water, and the coexistent phases to be:

1. Saturated solution;
2. Water vapor;
3. Solid salt.

In this case $m_{21} = 0$, and $m_{31} = 1$, wherefore the equations (10), (10*a*), (10*b*), give the slope of the solubility curve in the forms

$$(11)\quad \frac{\partial^2 h_1}{\partial m_{11}^2}\cdot\frac{dm_{11}}{d\theta} = \left(\frac{v_1 - v_2}{m_{11}} - \frac{\partial v_1}{\partial m_{11}}\right)\frac{\delta H}{\delta V} - \left(\frac{\eta_1 - \eta_2}{m_{11}} - \frac{\partial \eta_1}{\partial m_{11}}\right)$$

$$(11a)\quad = \left(v_3 - v_2 - \frac{\partial v_1}{\partial m_{11}}\right)\frac{\delta H}{\delta V} - \left(\eta_3 - \eta_2 - \frac{\partial \eta_1}{\partial m_{11}}\right)$$

$$(11b)\quad = \left(\frac{v_3 - v_1}{1 - m_{11}} - \frac{\partial v_1}{\partial m_{11}}\right)\frac{\delta H}{\delta V} - \left(\frac{\eta_3 - \eta_1}{1 - m_{11}} - \frac{\partial \eta_1}{\partial m_{11}}\right).$$

In any case the quantity $\delta H/\delta V$ is, of course, equal to the slope $dp/d\theta$ of the boundary curve in the p,θ-diagram. And it will not be overlooked that the function $\partial^2 h_1/\partial m_{11}^2$ is always positive for stable equilibrium.

An obvious comment on the general equation (10) is the following. From the three-phase system, in a state of equilibrium, suppose the third phase to be removed. For the remaining two-phase system, the equation of van der Waals cited at the beginning of this paper may be written

$$dm_{11} = dp\left(\frac{v_2 - v_1}{m_{21} - m_{11}} - \frac{\partial v_1}{\partial m_{11}}\right):\frac{\partial^2 h_1}{\partial m_{11}^2} - d\theta\left(\frac{\eta_2 - \eta_1}{m_{21} - m_{11}} - \frac{\partial \eta_1}{\partial m_{11}}\right):\frac{\partial^2 h_1}{\partial m_{11}^2}.$$

On comparing this equation with (10) we get (10) in the form

$$\frac{dm_{11}}{d\theta} = \frac{\partial m_{11}}{\partial p}\frac{\delta H}{\delta V} + \frac{\partial m_{11}}{\delta \theta}$$

$$= \frac{\partial m_{11}}{\partial p}\frac{dp}{d\theta} + \frac{\partial m_{11}}{\partial \theta},$$

where the total derivatives relate to the three-phase state, and the partials to the two-phase state. Thus, the quantity

$$m_{11},$$

which for a one-phase state is independently variable, and for a two-phase state becomes a function

$$m_{11}(p,\theta),$$

is altered on the appearance of a third phase to the implicit function of θ,

$$m_{11}\Big(p(\theta),\ \theta\Big),$$

the form in p,θ remaining unchanged.

Cornell University December, 1905.

ON THE DISPLACEMENT OF THE EQUILIBRIUM OF UNIVARIANT AND OF BIVARIANT SYSTEMS

BY PAUL SAUREL

If a chemical system be in equilibrium at a given temperature and under a given pressure, the change in the thermodynamic potential of the system due to a virtual change in which the masses of the phases vary while the temperature and the pressure remain constant will be equal to zero. If the thermodynamic potential of the system be denoted by Φ the condition of equilibrium may be written

$$\delta\Phi = 0. \tag{1}$$

The symbol δ is used to indicate differentiation with respect to the masses alone. Thus, if we denote the temperature by T, the pressure by Π and the mass of the j-th component which is present in the i-th phase by M_{ij}, we obtain $\delta\Phi$ by keeping T and Π constant and giving to the variables M_{ij} the increments δM_{ij}.

Let us consider two adjacent states of equilibrium of the system and let the temperature, the pressure and the masses in the first state be T, Π, M_{ij}, and in the second state $T + dT$, $\Pi + d\Pi$, $M_{ij} + dM_{ij}$. If the thermodynamic potential in the first state have the value Φ, in the second state it will have a value $\Phi + d\Phi$. If we apply the condition of equilibrium to each of these states we get, in addition to equation 1, the equation

$$\delta(\Phi + d\Phi) = 0. \tag{2}$$

From equations 1 and 2 we get at once the equation

$$\delta d\Phi = 0. \tag{3}$$

Just as equation 1 may be called the equation of equilibrium equation 3 may be called the equation of the displacement of equilibrium. From it we can find, in any particular case, the equations which connect the simultaneous changes in the temperature, the pressure, and the concentrations of the phases as the system passes from one state of equilibrium to an adjacent

state of equilibrium. In the present note we shall apply the general equation of displacement to the particular cases of univariant and of bivariant systems having any number of components. We shall thus obtain results which will include as special cases the formulae which van der Waals and Trevor have obtained for binary and for ternary systems.

Before applying equation 3 to univariant and to bivariant systems a few preliminaries are necessary. If we agree to use the symbol d_1 to indicate a change in which the masses M_{ij} alone vary and in which they receive increments $d'M_{ij}$ we may write

$$d\Phi = d_1\Phi + \frac{\partial\Phi}{\partial\Pi}\, d\Pi + \frac{\partial\Phi}{\partial T}\, d'T. \qquad (4)$$

If we denote the volume and the entropy of the system by V and by H and if we make use of the relations

$$\frac{\partial\Phi}{\partial\Pi} = V, \qquad \frac{\partial\Phi}{\partial T} = -H, \qquad (5)$$

we get

$$d\Phi = d_1\Phi + V d\Pi - H d'T. \qquad (6)$$

The equation of displacement 3 now takes the form

$$\delta d_1\Phi + \delta V . d\Pi - \delta H . d'T = 0. \qquad (7)$$

The thermodynamic potential of the system is the sum of the thermodynamic potentials of the phases. If there be r phases and if we denote the potential of the i-th phase by Φ_i we have

$$\Phi = \sum_{i=1}^{r} \Phi_i. \qquad (8)$$

If there be n components the thermodynamic potential Φ_i is a homogeneous function of the first degree in the masses M_{i_1}, $M_{i_2}, \ldots, M_{in}$. If then we write

$$F_{ij} = \frac{\partial\Phi_i}{\partial M_{ij}}, \qquad (9)$$

we have

$$\Phi_i = \sum_{j=1}^{n} F_{ij}\, M_{ij}. \qquad (10)$$

By differentiating this equation with respect to the masses M_{ij} and by making use of equation 9 we obtain the two equations

$$d_1\Phi_i = \sum_{j=1}^{n} F_{ij}\, dM_{ij}, \tag{11}$$

$$0 = \sum_{j=1}^{n} M_{ij}\, d_1F_{ij}. \tag{12}$$

We then obtain from 11

$$\delta d_1\Phi_i = \sum_{j=1}^{n} \delta F_{ij}\, dM_{ij}. \tag{13}$$

Moreover, since

$$\sum_{j=1}^{n} \delta F_{ij}\, dM_{ij} = \sum_{k=1}^{n}\sum_{j=1}^{n} \frac{\partial^2\Phi_i}{\partial M_{ij}\,\partial M_{ik}}\, \delta M_{ik}\, dM_{ij} = \sum_{j=1}^{n} d_1F_{ij}\, \delta M_{ij}, \tag{14}$$

it follows that we may also write

$$\delta d_1\Phi_i = \sum_{j=1}^{n} d_1F_{ij}\, \delta M_{ij}. \tag{15}$$

Since Φ_i is homogeneous and of the first degree in the masses M_{ij}, it follows that F_{ij} must be homogeneous and of the degree zero in the same variables. In other words, if m_{ij} be the mass of the j-th component which is present in the unit of mass of the i-th phase, we may say that F_{ij} is a function of the concentrations $m_{i_1}, m_{i_2}, \ldots, m_{i_n}$. Accordingly, if the virtual change to which δ refers be one in which the concentrations of the i-th phase remain constant, it follows that δF_{ij} will be equal to zero; equation 13 shows that $\delta d_1\Phi_i$ will also be equal to zero.

If we denote the thermodynamic potential of the unit of mass of the i-th phase by ϕ_i, equations 10, 11 and 12 enable us to write

$$\phi_i = \sum_{j=1}^{n} F_{ij}\, m_{ij}, \tag{16}$$

$$d_1\phi_i = \sum_{j=1}^{n} F_{ij}\, dm_{ij}. \qquad (17)$$

$$0 = \sum_{j=1}^{n} m_{ij}\, d_1 F_{ij}. \qquad (18)$$

By definition

$$\sum_{j=1}^{n} m_{ij} = 1, \qquad (19)$$

so that

$$\sum_{j=1}^{n} dm_{ij} = 0. \qquad (20)$$

Making use of equation 20 to eliminate dm_{in} from equation 17 we get

$$d_1\phi_i = \sum_{j=1}^{n-1} (F_{ij} - F_{in}) dm_{ij}. \qquad (21)$$

If we imagine that ϕ_i has been expressed as a function of the $n - 1$ concentrations $m_{i_1}, m_{i_2}, \ldots, m_{i\,n-1}$, equation 21 allows us to write

$$F_{ij} - F_{in} = \frac{\partial \phi_i}{\partial m_{ij}}. \qquad (22)$$

The volume of the system is equal to the sum of the volumes of the phases. If we denote the mass of the i-th phase by M_i and the volume of the unit of mass of this phase by v_i we may accordingly write

$$V = \sum_{i=1}^{r} M_i v_i. \qquad (23)$$

In like manner if η_i denote the entropy of the unit of mass of the i-th phase we have

$$H = \sum_{i=1}^{r} M_i \eta_i. \qquad (24)$$

ν_i and η_i are functions of the concentrations of the phase and it will be convenient to think of them as having been expressed in terms of the $n - 1$ concentrations $m_{i_1}, m_{i_2}, \ldots, m_{i\,n-1}$.

Let us now consider a univariant system consisting of $n + 1$ phases formed by means of n components. We shall begin by considering a virtual change in which the masses of the second and third phases vary while their concentrations remain constant and in which, moreover, the mass of the first phase remains constant while its concentrations vary; the remaining phases are not varied in any way. This virtual change may be described as consisting in the addition of a small mass of the second phase to the first and in the simultaneous removal from the first phase of a mass equal in magnitude to the added mass but having the composition of the third phase. The virtual change in question is defined by the equations

$$\delta M_1 = 0, \qquad \delta M_2 + \delta M_3 = 0 \tag{25}$$

$$-\delta M_{1j} = m_{2j}\,\delta M_2 + m_{3j}\,\delta M_3 = (m_{2j} - m_{3j})\,\delta M_2. \tag{26}$$

$$\delta M_{4\,j} = \delta M_{5j} = \ldots = \delta M_{n+1\,j} = 0. \tag{27}$$

Since the concentrations of all the phases except the first remain constant, the first term in the equation of displacement 7 reduces to $\delta d_1\Phi_1$. In virtue of equations 15 and 26 we have

$$\delta d_1\Phi_1 = \sum_{j=1}^{n} d_1F_{1j}\,\delta M_{1j} = -\delta M_2 \sum_{j=1}^{n} (m_{2j} - m_{3j})\,d_1F_{1j}. \tag{28}$$

Now since

$$\sum_{j=1}^{n} m_{2j} = 1 = \sum_{j=1}^{n} m_{3j}, \tag{29}$$

it follows that

$$m_{2n} - m_{3n} = -\sum_{j=1}^{n-1} (m_{2j} - m_{3j}). \tag{30}$$

If we make use of this result to eliminate $m_{3n} - m_{2n}$ from equation 28 we get

$$\delta d_1\Phi_1 = -\delta M_2 \sum_{j=1}^{n-1}(m_{2j}-m_{3j})(d_1F_{1j}-d_1F_{1n})$$

$$= -\delta M_2 \sum_{j=1}^{n-1}(m_{2j}-m_{3j})d_1(F_{1j}-F_{1n}). \qquad (31)$$

Finally, if we make use of equation 22, we get

$$\delta d_1\Phi_1 = -\delta M_2 \sum_{j=1}^{n-1}\sum_{k=1}^{n-1}(m_{2j}-m_{3j})\frac{\partial^2\phi_1}{\partial m_{1j}\partial m_{1k}}dm_{1k}. \qquad (32)$$

Moreover, since

$$V = \sum_{i=1}^{n-1} M_i v_i$$

we have for the virtual change considered

$$\delta V = M_1\,\delta v_1 + v_2\,\delta M_2 + v_3\,\delta M_3$$

$$= M_1 \sum_{j=1}^{n-1}\frac{\partial v_1}{\partial m_{1j}}\delta m_{1j} + (v_2 - v_3)\delta M_2. \qquad (33)$$

But since

$$M_1 m_{1j} = M_{1j} \qquad (34)$$

we have

$$M_1\delta m_{1j} = \delta M_{1j}. \qquad (35)$$

Making use of equation 26 we get

$$M_1\delta m_{1j} = -(m_{2j}-m_{3j})\delta M_2. \qquad (36)$$

We thus obtain

$$\delta V = \left[v_2 - v_3 - \sum_{j=1}^{n-1}\frac{\partial v_1}{\partial m_{1j}}(m_{2j}-m_{3j})\right]\delta M_2. \qquad (37)$$

In like manner

$$\delta H = \left[\eta_2 - \eta_3 - \sum_{j=1}^{n-1}\frac{\partial \eta_1}{\partial m_{1j}}(m_{2j}-m_{3j})\right]\delta M_2. \qquad (38)$$

If we substitute in equation 7 the values of $\delta d_1\Phi_1$, δV and

δH given by equations 32, 37 and 38 we obtain at once the equation

$$\left[v_4 - v_3 - \sum_{j=1}^{n-1}(m_{4j} - m_{3j})\frac{\partial v_1}{\partial m_{1j}}\right] d\Pi -$$

$$\left[\eta_4 - \eta_3 - \sum_{j=1}^{n-1}(m_{4j} - m_{3j})\frac{\partial \eta_1}{\partial m_{1j}}\right] dT$$

$$- \sum_{j=1}^{n-1}\sum_{k=1}^{n-1}(m_{4j} - m_{3j})\frac{\partial^2 \phi_1}{\partial m_{1j}.\partial m_{1k}} dm_{1k} = 0. \qquad (I)$$

We next consider a virtual change which differs from the one already used only in this respect: that the part previously played by the phase 3 is now played by the phase 4. This will lead to an equation in all respects similar to equation I; to obtain it, it is sufficient to replace the subscript 3 in equation I by the subscript 4. We may in like manner replace the subscript 3 by each of the subscripts 5, 6, . . . , $n + 1$. The resulting equations form with equation I a set of $n - 1$ equations connecting the changes of the $n - 1$ concentrations of the phase 1 with the changes in temperature and pressure. If the changes in temperature and pressure be given these $n - 1$ equations determine the corresponding changes in the $n - 1$ concentrations of the phase 1.

We might, in like manner, consider a virtual change involving the phases 1, 3, 4, in which the phases 3 and 4 should play the parts previously played by the phases 2 and 3. If the resulting equation be written down it will be found without difficulty that it is the result of subtracting from the equation that corresponds to the combination of phases 1, 2, 3 the equation that corresponds to the combination 1, 2, 4. In general, the equation corresponding to the combination 1, l, m, is a consequence of the equations corresponding to the combinations 1, 2, l, and 1, 2, m. It is thus evident that it is sufficient to consider only the $n - 1$ combinations (1, 2, 3), (1, 2, 4), (1, 2, 5), . . . , (1, 2, $n + 1$).

We should next have to consider a set of $n - 1$ virtual changes in which the phase 2 should play the part previously played by the phase 1. We should thus obtain a set of $n - 1$ equations connecting the changes in the $n - 1$ concentrations of the phase 2 with the changes in temperature and pressure. There will be a similar set of $n - 1$ equations for each of the remaining phases. We thus obtain $n + 1$ sets of $n - 1$ equations; all of these equations are of the same form as equation 1.

The $n - 1$ equations in one set determine the changes in the concentrations of the corresponding phase due to given changes in temperature and pressure. In a univariant system, however, the changes in temperature and pressure are not independent but are connected by the well-known Clapeyron-Clausius equation. This equation also can be derived without difficulty from equation 7. To obtain it, it is sufficient to consider a virtual change in which all the phases participate and in which the concentrations of each phase remain constant. The first term in Equation 7 vanishes and there results at once the Clapeyron-Clausius equation:

$$\frac{d\Pi}{dT} = \frac{\delta H}{\delta V}.$$

Thus the Clapeyron-Clausius equation and the $(n + 1)(n - 1)$ equations of the type I completely describe the displacement of the equilibrium of a univariant system.

In the preceding discussion the concentrations of all of the phases have been variable. If, however, the composition of any given phase be invariable, the $n - 1$ equations corresponding to that phase will disappear, for the virtual changes which enabled us to deduce these equations now become impossible.

For binary systems the equations of type I are due to Trevor.[1]

Let us next consider a bivariant system consisting of n phases formed by means of n components. We shall begin by considering a virtual change which consists in adding to the first phase a small mass of the second phase; the remaining

[1] Jour. Phys. Chem., 10, 99 (1906).

phases are not varied in any way. This virtual change is defined by the equation

$$\delta M_{1j} = - m_{2j}\, \delta M_2. \tag{39}$$

Since the concentrations of all the phases except the first remain constant, the first term in the equation of displacement 7 reduces to $\delta d_1\Phi_1$. In virtue of equations 15 and 39 we have

$$\delta d_1\Phi_1 = \sum_{j=1}^{n} d_1F_{1j}\, \delta M_{1j} = - \delta M_2 \sum_{j=1}^{n} m_{2j}\, d_1F_{1j}. \tag{40}$$

From equation 18 we have

$$0 = \sum_{j=1}^{n} m_{1j}\, d_1F_{1j}. \tag{41}$$

Multiplying this equation by δM_2 and adding to equation 40 we get

$$\delta d_1\Phi_1 = - \delta M_2 \sum_{j=1}^{n} (m_{2j} - m_{1j})\, d_1F_{1j}. \tag{42}$$

Now since

$$\sum_{j=1}^{n} m_{2j} = 1 = \sum_{j=1}^{n} m_{1j} \tag{43}$$

it follows that

$$m_{2n} - m_{1n} = - \sum_{j=1}^{n-1} (m_{2j} - m_{1j}). \tag{44}$$

If now we eliminate $m_{2n} - m_{1n}$ from equation 42 we get

$$\delta d_1\Phi_1 = - \delta M_2 \sum_{j=1}^{n-1} (m_{2j} - m_{1j})(d_1F_{1j} - d_1F_{1n})$$

$$= - dM_2 \sum_{j=1}^{n-1} (m_{2j} - m_{1j}) d_1(F_{1j} - F_{1n}). \tag{45}$$

Finally equation 22 enables us to write

$$\delta d_1\Phi_1 = - \delta M_2 \sum_{j=1}^{n-1} \sum_{k=1}^{n-1} (m_{2j} - m_{1j})\, \frac{\partial^2 \phi_1}{\partial m_{1j} \partial m_{1k}}\, dm_{1k}. \tag{46}$$

Moreover since

$$V = \sum_{i=1}^{n} M_i v_i,$$

we have for the virtual change under consideration

$$\delta V = M_1 \delta v_1 + v_1 \delta M_1 + v_2 \delta M_2$$

$$= M_1 \sum_{j=1}^{n-1} \frac{\partial v_1}{\partial m_{1j}} \delta m_{1j} + (v_2 - v_1)\delta M_2. \qquad (47)$$

Now since

$$M_1 m_{1j} = M_{1j},$$

it follows that

$$M_1 \delta m_{1j} = \delta M_{1j} - m_{1j}\delta M_1$$

$$= - m_{2j}\delta M_2 + m_{1j}\delta M_2$$

$$= - (m_{2j} - m_{1j})\delta M_2. \qquad (48)$$

Thus

$$\delta V = \delta M_2 \left[v_2 - v_1 - \sum_{j=1}^{n-1} (m_{2j} - m_{1j}) \frac{\partial v_1}{\partial m_{1j}} \right]. \qquad (49)$$

In like manner

$$\delta H = \delta M_2 \left[\eta_2 - \eta_1 - \sum_{j=1}^{n-1} (m_{2j} - m_{1j}) \frac{\partial \eta_1}{\partial m_{1j}} \right]. \qquad (50)$$

If we substitute in equation 7 the values of $\delta d_1\Phi_1$, δV and δH given by equations 46, 49 and 50 we obtain at once the equation

$$\left[v_2 - v_1 - \sum_{j=1}^{n-1} (m_{2j} - m_{1j}) \frac{\partial v_1}{\partial m_{1j}} \right] d\Pi -$$

$$\left[\eta_2 - \eta_1 - \sum_{j=1}^{n-1} (m_{2j} - m_{1j}) \frac{\partial \eta_1}{\partial m_{1j}} \right] dT$$

$$- \sum_{j=1}^{n-1} \sum_{k=1}^{n-1} (m_{2j} - m_{1j}) \frac{\partial^2 \phi_1}{\partial m_{1j}\, \partial m_{1k}} dm_{1k} = 0. \qquad (11)$$

We next consider a virtual change in which a small mass of the phase 3 is added to the phase 1. This yields an equation analogous to II; it can be obtained by replacing the subscript 2 in equation II by the subscript 3. In like manner we may replace the subscript 2 by 4, 5, . . . , n. The resulting equations form with II a set of $n - 1$ equations from which the changes in the $n - 1$ concentrations of the phase 1 can be determined when the changes in temperature and pressure are given.

We can, in like manner, consider a set of $n - 1$ virtual changes in which the phase 2 plays the part previously played by the phase 1. This yields a set of $n - 1$ equations from which the changes in the $n - 1$ concentrations of the phase 2 can be determined when the changes in temperature and pressure are given. Treating the remaining phases in the same way we obtain finally n sets of $n - 1$ equations of the type II. These equations determine the changes in the concentrations of the system due to given changes in temperature and pressure. Since, in a bivariant system, the temperature and the pressure can be varied arbitrarily, it follows that these equations completely describe the displacement of the equilibrium of a bivariant system.

If a given phase be of invariable composition the $n - 1$ equations corresponding to it will disappear, for the virtual changes which enabled us to get these equations now become impossible.

For binary and for ternary systems the equations of the type II are due to van der Waals.[1]

New York, December 11, 1905.

[1] Archives néerlandaises, 24, 15 (1890); 30, 267 (1896); (2) 2, 74 (1898). Die Continuität des gasförmigen und flüssigen Zustandes, 2, 13, 108, 112, 179 (1900).

THE SOLUBILITY OF GYPSUM IN SOLUTIONS OF AMMONIUM SULPHATE[1]

BY J. M. BELL AND W. C. TABER

The solubility of gypsum in ammonium sulphate solutions has been investigated by Droeze[2] at 9° C, by Cohn[3] at 22°.5 C, and by Sullivan[4] at 25° C. The results of Cohn and of Sullivan indicate that the solubility decreases at first with increasing amounts of ammonium sulphate, but as the concentration becomes large there is an increasing amount of gypsum in solution. Neither of these experimenters have observed the formation of any double sulphate of calcium and ammonium, although the compound $CaSO_4.(NH_4)_2SO_4.H_2O$ has been reported by Popp, Fassbender[5] and Ditte.[6] Fassbender evaporated a concentrated solution of ammonium sulphate containing gypsum and filtered off the mother-liquor at 40–50° C. It seems probable therefore that the double compound is not stable as low as 25° but is stable in the neighborhood of 40° C. As a double sulphate of calcium and potassium (syngenite) has already been found of the formula $CaSO_4.K_2SO_4.H_2O$, the solubility curve for the system, calcium sulphate, ammonium sulphate, water, has been determined at the higher temperature, 50° C.

A number of solutions were prepared by dissolving varying amounts of ammonium sulphate in water and adding an excess of gypsum. In addition three solutions were prepared, the first containing no gypsum, the second a solution about half saturated and the third a saturated solution of gypsum in water. To each of these three bottles an excess of ammonium sulphate was added. All these solutions were

[1] Published by permission of the Secretary of Agriculture.
[2] Ber. chem. Ges., Berlin., 10, 330 (1877).
[3] Jour. prakt. Chem. (2), 35, 43 (1887).
[4] Jour. Am. Chem. Soc., 27, 529 (1905).
[5] Ber. chem. Ges., Berlin, 9, 1358 (1876).
[6] Compt. rend., 84, 86 (1877).

placed in a thermostat at 50° and frequently agitated during several days. At the end of this time, the density of the solutions, the Ca-content and the SO_4-content, were determined and from these data both the volume-concentration and the mass-concentration may be computed. The compositions of the solutions are given in the following table and diagram.

Density	$(NH_4)_2SO_4$ per liter	$CaSO_4$ per liter
—	0	2.168
1.0026	15.65	1.609
1.0113	30.67	1.750
1.0440	91.6	2.542
1.0819	160.4	3.402
1.1108	221.6	4.068
1.1385	280.6	4.690
1.1653	340.6	5.084
1.1972	415.6	5.336
1.1964	416.5	5.354
1.2043	428.4	4.632
1.2187	479.4	3.524
1.2437	530.8	2.152
1.2480	558.0	1.986
1.2502	564.7	1 98
1.2508	566.0	1.08
1.2510	566.7	0.00

It is evident that there are three distinct solubility curves, one representing solutions in equilibrium with gypsum, one representing solutions in equilibrium with ammonium sulphate, and the third solutions in equilibrium with some other solid phase. The composition of this solid phase could not be determined by ordinary analysis on account of the difficulty of separating the concentrated mother-liquor from the fine crystals, so a method which has been suggested by Bancroft[1] has been adopted. To a solution in equilibrium with this new compound, solid calcium sulphate and ammonium sulphate were added. If the solids are added in the proportion in which

[1] Jour. Phys. Chem., 6, 181 (1902).

they are present in the solid phase, the composition of the solution will remain constant, but if they are added in any other proportion the composition of the solution will change. In this general case the amount of water contained in the gypsum may not be the same as the amount of water present as water of crystallization in the double sulphate. However, the amount of water added is so small in comparison to the amount of water already present and the amount of calcium sulphate added is so large in comparison to the amount already present that we have neglected this slight error. To about half a liter of a solution of the composition, 4.412 grams $CaSO_4$ and 449.7 grams $(NH_4)_2SO_4$ per liter, 13.22 grams $(NH_4)_2SO_4$ and 17.22 grams $CaSO_4.2H_2O$ were added; *i. e.*, in

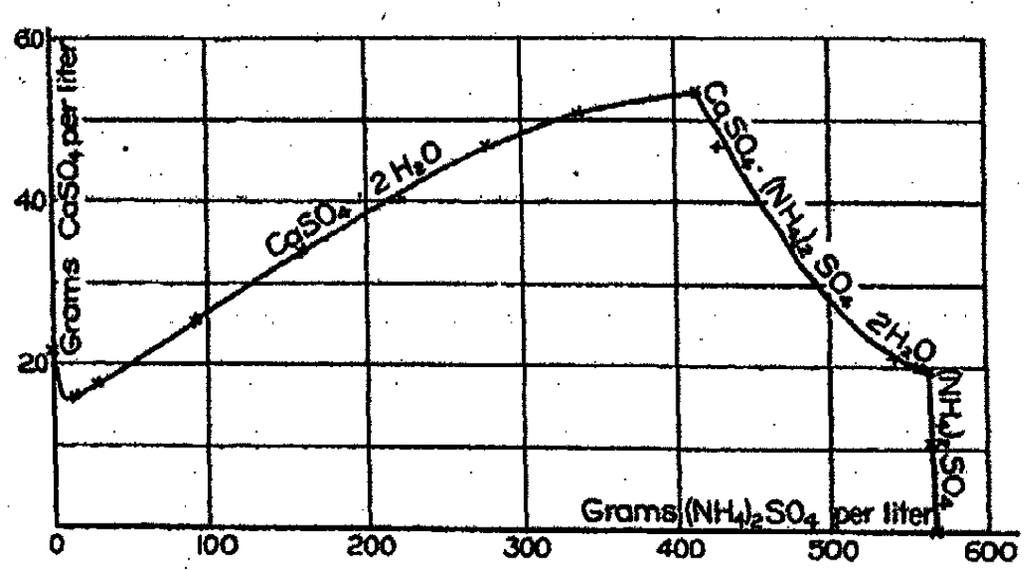


Fig. 1

equimolecular proportions. The solution, after two days at constant temperature about 50° C, was analyzed and found to have the same composition as before the addition of the two salts. We may then conclude that the composition of the double salt is $CaSO_4.(NH_4)_2SO_4.xH_2O$. The value of x has been determined graphically. The crystals of the double salt were freed as far as possible from the mother-liquor and the mixture showed, on analysis, 26.3 percent $CaSO_4$ and 40.7 percent $(NH_4)_2SO_4$. The composition of the mixture (D) and that of the supernatant solution (C) were plotted on a triangular diagram and the points joined by a line. The

composition of the solid phase lies upon the line produced, and also lies on the line representing mixtures containing the two sulphates in equimolecular proportions (AB). The

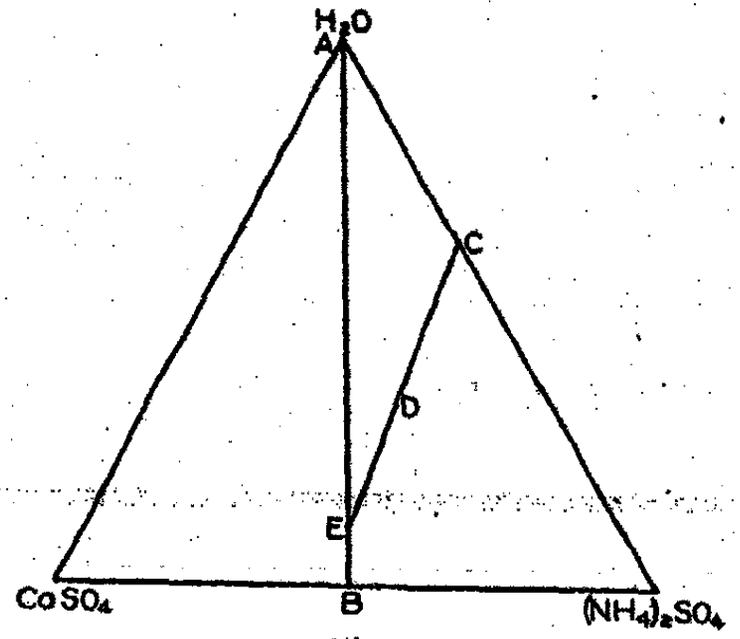


Fig. 2

intersection of these lines (E) represents therefore the composition of the solid phase, which is very close to

$$CaSO_4.(NH_4)_2SO_4.2H_2O.$$

This double compound is similar in formula to that described by Fritsche[1] for the double sulphate of sodium and calcium. It may also be noted that the error which was supposed to have been introduced by the addition of equimolecular proportions of gypsum and ammonium sulphate due to the water of crystallization of the gypsum amounts to zero, for the hydration of the double salt is the same as that of the salts added to the solution.

Bureau of Soils,
U. S. Department of Agriculture,
Washington, D. C.

[1] Jour. prakt. Chem., 72, 291 (1857).

NEW BOOKS

Die Elektrolyse geschmolzener Salze. *Zweiter Teil: Das Gesetz von Faraday; die Überführung und Wanderung der Ionen; das Leitvermögen. By Richard Lorenz.* (*Monographien über angewandte Elektrochemie, XXI. Band.*) *17 × 24 cm; pp. vi. + 257. Halle: Wilhelm Knapp, 1905. Price: 8.00 marks.*—In this volume the author discusses the behavior of fused salts with reference to Faraday's law, to the migration velocity, and to conductivity. Under Faraday's law the chapters are: Faraday's experiments on fused salts; the electrolytic equivalent and the current efficiency; apparatus; current efficiency at cathode; disturbing factors; metallic fog; colloidal gold solutions and the coloring of glass by metals; change of valency; the latent photographic image and the coloring of salts by cathode rays; the diffusion of metallic fog and the 'solubility' of metals in fused salts; effect of vapor-pressure on metallic fog and current losses; current efficiency at anode; test of Faraday's law with fused salts; test of Faraday's law with glass and rock crystal; the universally exact application of Faraday's law; fractional electrolysis of fused salts; effect of other substances on current efficiency; quantitative relation between current efficiency and current density.

Under transference and migration of ions, the headings of the chapters are: microscopic examination during the electrolysis of fused salts; migration of ions in fused and solid silver iodide; migration of ions during electrolysis of heated glass and quartz; electrolytic phenomena at the surface between two solvents; determination of transference number during the electrolysis of mixtures of fused salts.

Under conductivity the headings of the chapters are: metallic and electrolytic conductivity; pseudo-metallic or convective conductivity; conductivity of solid salts; conductivity of fused salts; conductivity of glass, porcelain and quartz; conductivity of oxides, sulphides and selenides.

The author has covered a great deal of ground and has covered most of it very well, so that the book will be invaluable for purposes of reference. The least satisfactory part is that on the fractional electrolysis of fused salts. The author is not at all clear in his own mind why these experiments went as they did and the reader suffers in consequence. *Wilder D. Bancroft*

Traité pratique d'Électrochimie. *By Richard Lorenz. Refondu, d'après l'Édition allemande. By Georges Hostelet. 14 × 23 cm; pp. vi + 323. Paris: Gauthier-Villars, 1905.*—This book combines a laboratory manual with a text-book on electrochemistry. Experiments are given illustrating the fundamental laws; the typical electrochemical reactions; electrolytic dissociation; electromotive forces and polarization; electrolytic analysis; and electrolytic production of substances. In an appendix there are some valuable tables in conductivity and electromotive forces.

While the book is admirable in many ways, there has been a complete failure to perceive the importance of studying variables and conditions. The chapter on electrolytic analysis is entirely out of date, rotating electrodes not

being used. In the theoretical part, p. 118, it would certainly have been better to have modified the statements about false equilibria. *Wilder D. Bancroft*

The Conductivity of Liquids; Methods, Results, Chemical Applications and Theoretical Considerations. *By Olin Freeman Tower. 15 × 23 cm; pp. iv + 182. Easton: The Chemical Publishing Co., 1905. Price: bound, $1.50.*—"This little treatise is designed to present in English a summary of the recent work on the electrical conductivity of liquids, and to aid, if possible, in the more complete adoption of the Kohlrausch system of units." The book is a modified English version of the volume by Kohlrausch and Holborn and will prove of distinct value to those who do not read German readily. Some things could well have been treated otherwise. It is a pity to calculate dissociation, p. 51, before discussing migration of ions. Some reference should be made to the importance of a very high frequency when determining the conductivity of concentrated solutions. The discussion of isohydric solutions is unsatisfactory. The work of Liebknecht and Nilsen, p. 121, should not have been quoted without making some statement as to the probable errors in the method. One admirable feature of the book is the recognition of the importance of non-aqueous solutions.

Wilder D. Bancroft

Elektrochemie. I., *Theoretische Elektrochemie und ihre physikalisch-chemischen Grundlagen. (Sammlung Göschen, No. 252.) By Heinrich Danneel. 10 × 15 cm; pp. 197. Leipzig: G. J. Göschen'sche Verlagshandlung, 1905. Price: 80 pfennigs.*—It is really surprising how much information the author has managed to compress into 196 tiny pages. The subject-matter is well treated and the experiments cited have been selected with care, except when the author talks of cupric chloride between platinum electrodes as a satisfactory instance of polarization. It would have been better to have taken zinc chloride and to have avoided the overlooked complications with cuprous chloride. In the reviewer's edition of Faraday's works the spelling is 'cation' though the author says that Faraday used the erroneous spelling 'cathion.'

Wilder D. Bancroft

Die Elektrochemie der organischen Verbindungen. *By Walther Löb. Dritte erweiterte und umgearbeitete Auflage von Unsere Kenntnisse in der Elektrolyse und Elektrosynthese organischer Verbindungen. 15 × 22 cm; pp. vii + 320. Halle: Wilhelm Knapp, 1905. Price: paper, 9 marks.*—In this third edition the subject-matter has been rearranged to a certain extent. In the first half we have the electrolysis of aliphatic and aromatic compounds, electrolysis with alternating current, and electrical endosmose. In the second half we have chapters on the effect of the spark discharge, the arc, the silent discharge, and the Tesla currents. Of special interest are the author's pyrogenic experiments while his unfinished work on syntheses by means of the silent discharge is likely to become of the first importance. *Wilder D. Bancroft*

Cours de Chimie physique, *suivi d' Applications à la Chimie et à la Biologie. Cours libre professé à la Faculté des Sciences de Paris. By Victor Henri. Premier Fascicule. 16 × 25 cm; pp. xii + 336. Paris: A. Hermann, 1906. Price: including the second part, 15 francs.*—The first number of this book contains the following chapters: general conditions for equilibrium in solutions;

electrical conductivity of solutions; electrolytic dissociation theory; electrical conductivity of non-aqueous solutions; application of dissociation theory to chemistry and biology; osmose and osmotic pressure of solutions; diffusion of solutions; cryoscopy; pressure and boiling-point measurements; solution, absorption and distribution; surface-tension and viscosity; optical properties of solutions; electrical phenomena in solutions.

In the preface the author announces his intention of always pointing out the explicit and implicit hypotheses, and their limitations. This is an admirable idea but it has not been carried out. There is nothing as to the effect of the heat of dilution on the osmotic pressure; there is no limitation as to the validity of the theory of isohydric solutions; the objections of Arrhenius to the solubility product are not stated; the effect of a third substance in changing the solubility of two partially miscible liquids is ignored; no reference is made to the abnormal taste and toxic properties of acid salts; the atomic weight of sodium, p. 215, is said to be 12; the Raoult formulation for the relation between concentration and vapor-pressure is used practically everywhere; and there is nothing to show that the molecular weight of the solvent liquid is of no importance. While the book may pass muster in France, it cannot be recommended. *Wilder D. Bancroft*

Spectroscopy. *By E. C. C. Baly. 13 × 19 cm; pp. xi + 568. New York: Longmans, Green & Co., 1905. Price: cloth, $2.80.*—"In the following pages I have endeavored to present the subject of spectroscopy from the practical side. As full details as possible have been given of the methods of working with the various types of instruments. In the many branches of applied spectroscopy as distinct from the statistical work, it has been quite impossible to deal with the great number of researches of the present time. Typical investigations have, therefore, been selected, both with the view of indicating the lines upon which present work is being carried on, and, further, in the hope, which I trust is not a vain one, that more workers may be encouraged to enter this fascinating and prolific field of research."

The headings of the chapters are: historical; the slit, prisms, and lenses; the complete prism spectroscope; the prism spectroscope in practice; the diffraction grating; the ruled grating in practice; the infra-red and ultra-violet regions; the application of interference methods to spectroscopy; the efficiency of the spectroscope; the photography of the spectrum; the production of spectra; the nature of spectra; the Zeeman effect; series of lines in spectra; change of wave-length; Rowland's grating ruling engines; recipes for solutions for silvering glass mirrors.

The thoroughly practical nature of the book may be well seen in the eleven pages, pp. 195–205, in which are given the details of the mounting of the 10-foot focus grating at University College. The volume is a worthy member of an admirable series. *Wilder D. Bancroft*

A Treatise on Chemistry. *By H. E. Roscoe and C. Schorlemmer. Third Edition. Vol. I: The Non-Metallic Elements. 14 × 22 cm; pp. xii + 931. New York: The Macmillan Company, 1905.*—The first edition appeared in 1877, the second in 1894 and the third in 1905. This last edition is just as valuable to-day as the first edition was in its day. Osmotic pressure and the elec-

trolytic dissociation theory appear early in the volume while there is a final chapter on the gases of the helium group. Moissan's investigations on the diamond are given in detail and reference is made to the manufacture of carborundum at Niagara Falls though curiously enough there is no reference to Acheson graphite. Baker's results on the vapor density of dried ammonium chloride are cited and Dixon's work on the explosion wave. The general arrangement and the style remains much the same in the preceding editions. Both are familiar to all English-speaking chemists.

Wilder D. Bancroft

Radium and Radio-active Substances. *Their Application Especially to Medicine. By Charles Baskerville. 16 × 24 cm; pp. 164. Philadelphia: Williams, Brown and Earle, 1905.*—"This book emphasizes . . . the application of radio-active substances in medicine. The writer is not in a position to harmonize the contradictory evidence given in reputable medical journals as to the therapeutic uses of the salts of radium, consequently the observations have been impartially reported."

"As many physicians will have neither the time nor the opportunity to study the larger works, sufficient of the general subject has been presented for a fairly clear conception of our present knowledge of these startling, perhaps revolutionary, phenomena."

The reviewer is not qualified to judge the value of this book to physicians. The chemist will find in it a sketchy outline of the subject.

Wilder D. Bancroft

Ueber Heizwertbestimmungen mit besonderer Berücksichtigung gasförmiger und flüssiger Brennstoffe. *By Theodor Immenkötter. 16 × 23 cm; pp. vii + 97. München and Berlin: R. Oldenbourg, 1905. Price: paper, 3 marks.*—This is really a pamphlet describing the Junker continuous calorimeter. The first section treats of previous forms of calorimeters while the remaining three deal entirely with the Junker calorimeter and its all-round usefulness.

Wilder D. Bancroft

Les petits Métaux. *By P. Truchot. (Encyclopédie scientifique des Aide-Mémoire). 12 × 19 cm; pp. 189. Paris: Gauthier-Villars, 1905.*—This volume deals with the metals, titanium, tungsten and molybdenum. Since the general style of these volumes is well-known, a reference to the subject-matter will suffice.

Wilder D. Bancroft

REVIEWS

The object of this department of the Journal is to issue, as promptly as possible, critical digests of all Journal articles that bear upon any phase of Physical Chemistry.

General

A revision of the atomic weight of strontium. *T. W. Richards. Proc. Am. Acad.*, 40, *603; Zeit. anorg. Chem.*, 47, *145* (*1905*).—In 1895-6 work was carried out in the author's laboratory on the analysis of strontium chloride. The result for the atomic weight of strontium did not agree with that obtained from the analysis of strontium bromide and the work was not published although no source of error could then be found. By putting in the new value for chlorine 35.473 (Ag = 107.930) the atomic weight of strontium becomes 87.663 from the bromide analyses and 87.661 from the chloride analyses. This is a striking agreement and furnishes most gratifying confirmation of the accuracy both of the earlier work and of the new value for chlorine. *W. D. B.*

Sources of error in the determination of the atomic weight of nitrogen. *T. W. Richards. Proc. Am. Phil. Soc.*, 43, *116* (*1904*).—It is claimed that Scott did not purify sufficiently the bromine used in preparing his ammonium bromide. Hardin and Hibbs worked with such small quantities that their results of 14.01 cannot claim any special accuracy. Work in the author's own laboratory leads him to believe that the atomic weight of nitrogen is pretty certainly at least 14.02 and probably nearly 14.04. *W. D. B.*

The interdependence of the atomic weights and the electrochemical equivalents. *A. Reuterdahl. Trans. Am. Electrochem. Soc.*, 7, *187* (*1905*).—The author postulates, apparently as a new result, that the ampere hours per gram of any substance give a constant when divided by the valency and multiplied by the atomic weight in grams. This is nothing more than the old statement that equal ampere hours precipitate equivalent weights of different ions. The author plots the data using polar co-ordinates and then indulges in speculations. *W. D. B.*

The specific heat of carbon at high temperatures. *L. Kunz. Drude's Ann.*, 14, *309* (*1904*).—Carbon in the form of pulverized beech-wood is used for the measurements. This was treated in an electric furnace. The ice calorimeter was employed for the heat estimated. The specific heat at 1000° is found to be 0.363, lower than either Weber's or Violle's results for graphite. *H. T. B.*

F. E. Neumann's method for determining the thermal conductivity of poorly conducting bodies. *H. Hecht. Drude's Ann.*, 14, *1008* (*1904*).—The conductivity of marble, glass, sandstone and gypsum is determined by the rate of fall or rise in temperature in low vacuum and at ordinary pressures. Both spheres and cubes of the substances were used. *H. T. B.*

The accumulation of solar heat in liquids. *A. v. Kalecsinsky. Drude's Ann.*, 14, *843* (*1904*).—The author continues his study of the warming of salt water layers under fresh water by the trapping of the sun's rays. Wooden tubes were made and solutions of various salts taken. Fresh water itself becomes warmed when covered by a layer of oil. The explanation is a physical rather than a chemical one. Other natural salt lakes have been found since the publication of the author's first paper. *H. T. B.*

Expressions for the thermal properties of matter. *A. Batschinski. Drude's Ann.*, 14, *288* (*1904*).—Developing van der Waals equation the author deduces a number of expressions for the thermal properties of matter, treating first the external and second the internal heat of vaporization. *H. T. B.*

One-Component Systems

On boiling oxygen. *A. Bestelmeyer. Drude's Ann.*, 14, *87* (*1904*).—The author endeavors to determine what part superheating plays in the determination of the boiling-point of oxygen. Liquid oxygen is surrounded by liquid air and the boiling continued by means of an electrically heated spiral. It is found that the superheating always exists but that it varies considerably with the method of heating. In some cases it amounted to over a degree.

H. T. B.

Investigations of critical density and the theory of Andrews-van der Waals. *G. Bakker. Drude's Ann.*, 15, *543* (*1904*).—The author considers that the simplest way is to regard the critical point as an enlargement of the capillary layer and shows that this does not necessarily conflict with the ideas of Andrews, James Thomson and van der Waals. The paper is a very important one in that it presents the subject from a new point of view. The experimental evidence existing at present goes to substantiate the author's views.

H. T. B.

Thermal expansion of hydrogen and carbon dioxide under constant pressure. *T. W. Richards and K. L. Mark. Proc. Am. Acad.*, 41, *117* (*1905*).—In the improved apparatus the pressure of a gas can be measured with an accuracy of one thousandth of a millimeter of mercury. From experiments at 32.38° and 0° the coefficient of expansion under constant pressure is found to be 0.0036609 for hydrogen and 0.0037282 for carbon dioxide. By a misprint the room is said to have been kept at a constant temperature at 200° instead of 20.0°.

W. D. B.

The density of nitrogen and its dependence on the pressure at the temperature of liquid air. *A. Bestelmeyer and S. Valentiner. Drude's Ann.*, 15, *61* (*1904*). —Measurements are made under pressures from 16 to 32 cm. of mercury at temperatures of 81° to 85° absolute. A linear relation between the product pv and the pressure is shown. Comparing their results with Chappuis' numbers for the coefficient of expansion between 0 and 100° for $p = 0$ it is shown that the scale of the platinum thermometer used was 0.2° too high in liquid air. The absolute zero becomes 273.04.

H. T. B.

The dependence of the ratio C_p/C_v of the specific heats of nitrogen on the pressure at liquid air temperature. *S. Valentiner. Drude's Ann.*, 15, *74* (*1904*).

—The author uses the method of Röntgen for measuring the ratio C_p/C_v at different temperatures and pressures. The value of the ratio is given as $1.3997 + 0.07812 \frac{p}{S}$ where p is the pressure in the tube and S is the normal pressure as given by Baly. Taking the formula for the density of hydrogen obtained by the author and Bestelmeyer (preceding review) the values of the two specific heats are given. *H. T. B.*

The variation of specific gravity. I. *G. W. A. Kahlbaum. Drude's Ann.*, 14, *578* (*1904*).—The effect of drawing a wire on its specific gravity is tried for platinum. The results confirm the author's previous work on the effect of pressure on the specific gravity. It appears that this increases with pressure up to a maximum and then decreases again for very high pressure, over 10,000 atmospheres. *H. T. B.*

A volumometer for large temperature intervals. *L. Zehnder Drude's Ann.*, 15, *328* (*1904*).—By changes made in his volumometer previously described (7, 599) the author devises one which will determine small volumes over the range —38.8 to +357° C. As an example the density of rhombic and monoclinic sulphur is determined, giving for the former 2.091 at 21.4° and the latter 1.915 at 103° C. *H. T. B.*

The elastic constant and hardness of amorphous quartz. *F. A. Schulze. Drude's Ann.*, 14, *384* (*1904*).—A short paper on the determination of some of the physical constants of amorphous quartz including the dielectric constant. *H. T. B.*

Two-Component Systems

The isomorphism and thermal properties of the feldspars. *A. L. Day and E. T. Allen. Am. Jour. Sci.* (*4*), 19, *93* (*1905*).—Neither the heating- nor the cooling-curve for vitreous borax showed any break as the borax changed from a hard glass to a thin liquid. Pounding the outside of the crucible with an electric hammer caused the borax to crystallize on cooling. Starting with the crystallized material a sharp melting-point could be obtained at 742°. Experiments were then made on mixtures of artificial (pure) anorthite and albite. Crystalline anorthite melts at 1532°. Crystalline albite melts so slowly that no definite point can be obtained. It can readily be heated several hundred degrees above its probable melting-point and the glass is quite as viscous as the solid. Over the range that can be followed anorthite and albite form a continuous series of solid solutions, the solid and liquid phases in equilibrium having practically identical compositions. *W. D. B.*

The microstructure of silicon and alloys containing silicon. *A. R. Albro. Trans. Am. Electrochem. Soc.*, 7, *251* (*1905*).—Forty-six photo-micrographs of silicon, ferro-silicon and other silicon alloys are given. No annealings were made and it is therefore probable that the work will have to be repeated from beginning to end. *W. D. B.*

Application of the hypothesis of dissolved ice to the freezing of water and of dilute solutions. *C. S. Hudson. Phys. Rev.*, 21, *16* (*1905*).—The author adopts Röntgen's hypothesis that water near the freezing-point contains dis-

solved ice. He then says that this will account for the constant freezing-point of pure water and for the lowering of the freezing-point of dilute solutions; but he does not make clear what he means by this. We cannot assume that he believes that water would not have a constant freezing-point if it did not contain dissolved ice. If he does not believe this, there is nothing new in the paper. The laws for the lowering of the freezing-point apply equally well to associated and to normal liquids. *W. D. B.*

The basic properties of oxygen at low temperatures. *D. McIntosh. Jour. Chem. Soc.*, 87, 784 (1905).—The author has prepared addition products of bromine and chlorine with methyl alcohol, ethyl alcohol, ethyl ether, acetone and ethyl acetate. With methyl ether and bromine, the solid compound $(CH_3)_2O.Br_2$ was formed while an addition compound can also be obtained from acetaldehyde and chlorine. *W. D. B.*

The heat of solution of aluminum bromide in ethyl bromide. *H. E. Patten. Trans. Am. Electrochem. Soc.*, 7, 177 (1905).—The author has determined the heats of solution and dilution for aluminum bromide in ethyl bromide solution. As the solvent and solute react slowly with each other even at 0°, it was impossible to make vapor-pressure determinations. *W. D. B.*

Multi-Component Systems

Colloids. *W. R. Whitney. Trans. Am. Electrochem. Soc.*, 7, 225 (1905).—An experimental lecture on colloids very similar to the one delivered by Noyes at Philadelphia (9, 433). Attention is called to the bearing which the study of colloids has on "the production of all precipitates in solutions, the chemistry of proteids, blood immunity and infection, dyeing of textile fabrics, the coloring of glass, the settling of slimes, the cementing of clays, electrical endosmose, etc." *W. D. B.*

Studies on the properties of an unproductive soil. *B. E. Livingston, J. C. Britton and F. R. Reid. Bureau of Soils Bulletin*, 28 (1905).—It is shown "that Takoma soil contains a water-soluble non-volatile substance or substances, probably organic in their nature, which are toxic to wheat plants, causing a stunting of their growth. The toxicity of the soil is corrected by the use of a stable manure, green manure, leaves of sumac, oak, etc., tannic acid, pyrogallol, calcium carbonate, ferric hydrate, and carbon black. Tannic acid and pyrogallol probably act chemically upon the toxic bodies, rendering them harmless, calcium carbonate may act chemically or as an absorbent, while ferric hydrate and carbon black probably act merely as absorbents. *W. D. B.*

Some technical applications of the phase rule. *W. Meyerhoffer. Verh. des Vereins für Beförderung des Gewerbfleisses*, 1905, 159.—In this address the author discusses fractional distillation and the Solvay soda process as examples of the application of the phase rule in technical work. *W. D. B.*

Preparation of pure praseodymium. *C. Baskerville. Zeit. anorg. Chem.*, 45, 86 (1905).—The author suggests that Meyer and Turrentine must have neglected some of the details in the method of purifying praseodymium by the double alkali carbonate method. He gives further directions as to the use of the method. *E. S. S.*

Utilization of blast-furnace gases in connection with the electric smelting of iron. *A. J. Rossi. Trans. Am. Electrochem. Soc.*, 7, 199 (*1905*).—The author estimates that the utilization of blast-furnace gases would give an available supply of about 450 H. P. hours per ton of iron made. In the discussion that followed, this optimistic view was not shared by many of the speakers.

W. D. B.

Osmotic Pressure and Diffusion

The diffusion of argon and helium. *R. Schmidt. Drude's Ann.* 14, 801 (*1904*).—The diffusion coefficient comes out 0.25405 by experiment for the two gases using Maxwell's method. Calculating from the kinetic theory of gases using the formula of O. E. Meyer the coefficient works out to be 0.2537 at 15° and standard pressure.

H. T. B.

Electromotive Forces

The polarization of galvanic cells in the presence of solid salt. *W. Jaeger. Drude's Ann.*, 14, 726 (*1904*).—It is shown in particular for dilute solutions that the magnitude of the polarization can be calculated from an equation. The polarization is determined by the diffusion constant, the velocity of solution and of crystallization. It is shown that for strong solutions the more finely the salt is divided, the smaller is the polarization. The danger in using cadmium cells from this cause has been overestimated.

H. T. B.

A low voltage standard cell. *G. A. Hulett. Trans. Am. Electrochem. Soc.*, 7, 333 (*1905*).—The author makes up a cell Cd | $CdSO_4$ | Cd amalgam. The electromotive force is 0.05175 volt at 20°.

W. D. B.

The Nernst-Planck theory of the potential between dilute solutions. *K. R. Johnson. Drude's Ann.*, 14, 995 (*1904*).—This paper is an extension of the mathematical treatment by Planck of the potential difference between two solutions. Where Planck took the special case that the valencies of the positive and negative ions in the two solutions were all equal, the author takes the case where the two positive and two negative are alone equal.

H. T. B.

The present status of the Edison storage battery. *A. E. Kennelly and S. E. Whiting. Trans. Am. Electrochem. Soc.*, 6, 11, 135 (*1904*).—The current efficiency of the Edison cell on a four-hour cycle is 75 percent and the voltage efficiency 70 percent, giving an energy efficiency of about 50 percent. It is claimed that this is more than offset by the large output at heavy discharge rates, by the low depreciation in capacity, and by the durability under severe treatment.

W. D. B.

The Edison storage battery. *M. de K. Thompson, Jr., and H. K. Richardson. Trans. Am. Electrochem. Soc.*, 7, 95 (*1905*).—It is believed that "the nickel plate when fully charged is some high oxide of nickel not yet isolated. This is reduced during discharge to Ni_2O_3 and NiO, both of which probably exist together at the second constant part of the discharge curve. When the battery is fully discharged the nickel oxide is reduced to nickel."

In 6 percent solution the iron electrode loses its capacity. The temperature coefficient varies with the concentration of the caustic potash but the electro-

motive force of the fully-charged cell does not. Gas analysis shows that the charging efficiency of the iron plate is 20 percent higher than that of the nickel plate. More material oozes from the plate the more concentrated the solution. *W. D. B.*

A study of the materials used in standard cells and their preparation. *H. S. Carhart and G. A. Hulett. Trans. Am. Electrochem. Soc.*, 6, *11*, *109* (*1904*). —Reviewed (9, 346) from *Zeit. phys. Chem.*, 49, *483* (*1904*).

The electrochemical series of metals. *L. Kahlenberg. Trans. Am. Electrochem. Soc.*, 6, *11*, *53* (*1904*).—The author has determined the apparent potential differences of many of the metals against *n*/10 LiCl in varying mixtures of pyridine and water. There are many changes of position when one deduces the electrochemical series from these experiments. *W. D. B.*

The polarization of the Volta effect. *W. Gaede. Drude's Ann.*, 14, *641* (*1904*).—A review is given of the contact and chemical theories of the Volta potential. Measurements are made between zinc and copper plates in air. The zinc plate is then removed and connected with the positive pole of a Wimshurst machine, the discharge taking place to a platinum point connected to the negative pole. On testing again the contact potential is found to have decreased but gradually returns to its original value. Connecting the zinc to the negative pole for a while causes an increase. The effect is compared with electrolytic polarization. *H. T. B.*

Reversible and irreversible electrolytic polarization. *W. S. Franklin and L. A. Freudenberger. Trans. Am. Electrochem. Soc.*, 7, *33* (*1905*).—The authors divide the potential difference necessary to force a given current through a given electrolytic cell into three parts: that due to the resistance of the electrolyte, that due to reversible polarization, and that due to irreversible polarization. They then make experiments on horizontal copper electrodes in an acidified copper sulphate solution. Their results point to an irreversible polarization of about 0.1 volt. Working as they do with horizontal electrodes and without stirring, they seem to have selected ideal conditions for not getting simple results. *W. D. B.*

On ozone. *S. Jahn. Zeit. anorg. Chem.*, 42, *203* (*1904*).—A current of oxygen containing 7 per cent ozone was passed through hydrochloric acid solutions in which colloidal platinum was present as catalytic agent. The chlorine set free was measured in another vessel as hydrochloric acid. From the known potential of chlorine it is possible to calculate the ozone potential. This figures out to 1.544 volts measured against the hydrogen electrodes and agrees admirably with the experimental value of 1.54 volts obtained by Gräfenberg when using platinized platinum electrodes in normal sulphuric acid. *W. D. B.*

On Billitzer's method for determining absolute potential differences. *H. M. Goodwin and R. B. Sosman. Trans. Am. Electrochem. Soc.*, 7, *83* (*1905*).—"The present investigation was undertaken in order to obtain a confirmation of Billitzer's results on absolute potentials by the method of deflections of a minute metallic electrode suspended in various solutions under the influence of an electric current. The results obtained have failed completely to confirm the

measurements made by him, and we are forced to the conclusion that the method proposed is not to be relied upon for the purpose for which it was developed. This conclusion is further confirmed by the results obtained by Blake on the migration of colloids, who has also failed to confirm Billitzer's measurements using this method.

"So far as our experiments go, it would seem that most of the phenomena observed may be explained on the assumption of the negative migration of gaseous particles in the liquid, as first demonstrated by Quincke in 1861."

W. D. B.

Diameter of molecules. *J. Bernstein, Drude's Ann.*, 14, *172* (*1904*).—Considering the layer of HgO in the Lippmann electrometer of molecular thickness, the electrical "double layer" is found to be about 6.18 x 10—7 mm. The radius of action of a molecule is about ten times its own radius. *H. T. B.*

Change of the Peltier effect with the temperature. *E. G. Bausenwein. Drude's Ann.*, 15, *213* (*1904*).—Taking the expression for the Peltier effect as $P = T\frac{dE}{dT}$ by observing E and T the value of P can be calculated. A current of Cu–Fe–Cu is used and a strong electric current passed. A constantan wire was soldered to each Cu–Fe junction and brought to a galvanometer. The whole combination can be raised to 800° in an electric furnace. Tables and curves are given for both the thermoelectric force and Peltier effect. It is found that a marked change occurs in the Peltier effect at 700° C., and that these curves have at the start a parabolic form. The known inversion of iron at about 750° C., may be the cause of the change in the curves at the higher temperature. *H. T. B.*

An electrolytic switch. *W. S. Horry. Trans. Am. Electrochem. Soc.*, 7, *237* (*1905*).—In a continuous current circuit possessing inductance, the voltage rises across the break when a switch is opened. The author uses an aluminum cell in order to prevent an undue rise of potential. *W. D. B.*

Electrolysis and Electrolytic Dissociation

A determination of the electrochemical equivalent of silver. *G. van Dijk and J. Kunst. Drude's Ann.*, 14, *569* (*1904*).—A tangent galvanometer and the usual form of voltameter was employed. A table of results is given showing that the several determinations were made with good agreement. The value obtained is 0.0111823. It is to be hoped that the authors will give a more complete account of the measurements if it is to stand as an absolute value.

H. T. B.

The lead voltameter. *A. G. Betts and E. F. Kern. Trans. Am. Electrochem. Soc.*, 6, *II*, *67* (*1904*).—Experiments are published to show that a very satisfactory voltameter can be obtained by using lead electrodes in a solution containing 8.5 percent $PbSiF_6$, 2.5 percent H_2SiF_6 and one part gelatine to two thousand of solution. A current density of 25–35 amperes per square foot may be used, and a platinum cathode may be substituted for a lead one if desired.

W. D. B.

The silver voltameter. *K. E. Guthe. Trans. Am. Electrochem. Soc.*, 6, *II*, *85* (*1904*).—Reviewed (9, 609) from *Phys. Rev.*, 19, 138 (1904).

Diaphragm cell for electrolysis of sodium chloride solution. *C. P. Townsend. Trans. Am. Electrochem. Soc.*, 7, 63 (1905).—This is another application of the principle embodied in the Hargreaves and Bird cell. One face of the gauze cathode is against the diaphragm while the other face is immersed in oil. As the solution comes through the diaphragm, the caustic soda is carried out into the oil by the bubble of hydrogen. Current densities of 100 amperes per square feet are to be used. *W. D. B.*

The rotating diaphragm. *W. D. Bancroft. Trans. Am. Electrochem. Soc.*, 7, 171 (1905).—With a rotating graphite diaphragm in a copper sulphate solution, a considerable portion of the current passes through the diaphragm without developing any polarization because the copper deposited on the side toward the anode is at once dissolved from the side toward the cathode, the net result being no apparent precipitation of copper. *W. D. B.*

The chemistry of electroplating. *W. D. Bancroft. Trans. Am. Electrochem. Soc.*, 6, *II*, 27 (1904).—A preliminary notice of the paper published in full (9, 277).

The electrolytic precipitation of silver. *R. C. Snowdon. Trans. Am. Electrochem. Soc.*, 7, 143 (1905).—Published (9, 392).

The electrolytic precipitation of nickel on nickel. *R. C. Snowdon. Trans. Am. Electrochem. Soc.*, 7, 301 (1905).—Published (9, 399).

Chromium and the electrolysis of chromic acid. *H. R. Carveth and B. E. Curry. Trans. Am. Electrochem. Soc.*, 7, 115 (1905).—Abstract of a paper published (9, 353).

Electrodeposition of metals on aluminum. *A. Lodyguine. Trans. Am. Electrochem. Soc.*, 7, 153 (1905).—The author cleaned aluminum plates in hydrochloric acid and then in caustic soda, afterwards precipitating copper from a sulphate solution. With small plates he obtained a coating of copper which passed the bending tests. Apparently no experiments were made to determine the effect of weathering. Various other people have done as much and more than this. Antimony was deposited on copper from a solution of the sulphide in sodium monosulphide. *W. D. B.*

Reduction of different oxides of lead by electric current. *A. Lodyguine. Trans. Am. Electrochem. Soc.*, 7, 221 (1905).—When lead peroxide is made cathode in a solution of sodium chloride and sulphuric acid the following layers can be obtained if the current is stopped at the right moment: spongy lead Pb_2O, litharge, $PbSO_4$, $PbCl_2$, PbO_2. It was not explained why such an electrolyte was desirable. *W. D. B.*

Notes on economic temperatures of copper-refining. *C. F. Burgess. Trans. Am. Electrochem. Soc.*, 7, 51 (1905).—It had been stated by the reviewer (8, 73) that the effect due to the distance between two copper electrodes in acidified copper sulphate solution can be eliminated if the voltage necessary to produce a given current density at any given temperature is expressed as a percentage of the voltage necessary to produce the same current density at an arbitrarily selected standard temperature. The author points out very properly

that this is true only in case there is no counter-electromotive force and no 'transfer resistance.' In the criticism on p. 54 the author has, however, overlooked the fact that one centimeter does not differ much from one-half inch. The author reached no conclusion as to the cause of the apparent transfer resistance which his experiments seem to show. *W. D. B.*

The aluminum electrolytic condenser. *C. I. Zimmerman. Trans. Am. Electrochem. Soc., 7, 309 (1905).*—This is a continuation of the previous paper (9, 73) and deals especially with unsymmetrical condensers and with polyphase condensers. *W. D. B.*

The electrolysis of fused salts. *R. Lorenz. Trans. Am. Electrochem. Soc., 6, II, 150 (1904).*—This is a condensed account of the results obtained in the author's laboratory by Helfenstein, Czepinski, Auerbach, Grünhauer, Schultze, Appelberg, Weber, Suchy, Sacher and others. *W. D. B.*

Electrolytic conduction. *J. W Richards. Trans. Electrochem. Soc., 6, II, 152 (1904).*—The author believes that metallic and electrolytic conduction are one and the same thing. In an experiment with the cell Zn | solid $ZnCl_2$ | fused $ZnCl_2$ | solid $ZnCl_2$ | Zn the author observed no change at the electrodes after a current of 100 micro-amperes had passed for fifteen minutes. He draws the conclusion that no change occurred. *W. D. B.*

Conduction in fused and solid electrolytes. *J. W. Richards. Trans. Am. Electrochem. Soc., 7, 71 (1905).*—According to the author "the electric current at the electrodes disturb the chemical equilibrium and introduces, or at least accentuates, a new phase in the melt; it extracts acid at the anode and leaves the melt there with a basic phase; it extracts base at the cathode and leaves the melt there with an acid phase. These two new phases diffuse with great rapidity in the melt, and thus carry the acid ingredient towards the anode and the basic ingredients towards the cathode. They are also capable of reacting upon the substances separated upon the electrodes, the velocity of this reaction increasing rapidly with the temperature, and when they recombine with them as fast as they are separated upon the electrodes, the current passes without apparent electrolysis." *W. D. B.*

Chlorine in metallurgy. *J. Swinburne. Trans. Am. Electrochem. Soc., 6, II, 80 (1904).*—A description of the Swinburne-Ashcroft process for treating sulphide ores with chlorine, recovering the sulphur. The mixed chlorides are treated with water and the lead chloride is electrolyzed (fused?). From the solution containing the chlorides of zinc, iron and manganese, the iron and manganese, are precipitated by zinc oxide, the zinc chloride solution is evaporated, and electrolyzed. No figures are given for voltage or yield in the electrolysis of fused zinc chloride. As run commercially, the zinc chloride is not electrolyzed, but is sold as such. *W. D. B.*

Electrolysis and catalysis. *W. Ostwald. Trans. Am. Electrochem. Soc. 6, II, 187 (1904).*—The author points out that reactions at the electrodes may often be considered as taking place in one or more steps and that in many cases there may be different reaction products depending on the conditions. The introduction of a suitable catalytic agent may easily make it possible to prepare otherwise instable compounds. *W. D. B.*

Revision of the theory of electrolysis. *H. S. Carhart. Trans. Am. Electrochem. Soc.*, 7, 15 (1905).—A historical sketch of the different views on electrolysis, starting with van Troostwijk and Deimann in 1789. *W. D. B.*

Production of silicon in the electric furnace. *F. J. Tone. Trans. Am. Electrochem. Soc.* 7, 243 (1905).—Silica and coke are heated in a vertical resistance furnace. The fused silica flows down into a lower chamber whence it is tapped and cast into pigs. The commercial product melts at 1430° and has a specific gravity of 2.34. It has a hardness between six and seven on the scale and is quite brittle. Even at 1300° it is not oxidized in the air though it oxidizes readily when the temperature is raised much above this. *W. D. B.*

Reduction of titaniferous ores. *A. Lodyguine. Trans. Am. Electrochem. Soc.*, 7, 157 (1905).—The method and the furnace were not described but the author asserts that he can smelt a titaniferous ore in his electric furnace so as to furnish an iron containing anywhere from traces up to 17 percent of titanium. It is estimated that to make 2000 pounds of steel would require 1570 K. W. hours. *W. D. B.*

Fluidity and conductivity of concentrated salt solutions below 0°. *W. Hechler. Drude's Ann.* 15, 157 (1904).—From the interpolation formula of Déguisne deduced from the conductivity of dilute solutions Kohlrausch showed that at —39° the internal friction of water should be infinitely great. Since dilute solutions cannot be cooled far below 0° the author studies concentrated solutions. Poiseuille's method was adopted for determining the fluidity and Kohlrausch's method for the resistance. *H. T. B.*

Electrolytic dissociation in alcoholic solutions. *T. Godlewski. Bull. Acad. Sci. Cracovie*, 1904, 239.—The dilution law holds fairly well for solutions of organic acids in alcohol; the order of the constants is not the same as in aqueous solutions. In aqueous alcohol solutions the dilution law holds over the whole range for salicylic, cyanacetic, and bromacetic acids. The first addition of alcohol decreases the dissociation constants but slightly, while they fall off very rapidly as the alcohol concentration increases from 90 percent to 100 percent. *W. D. B.*

Phenolphthaleine and the theory of indicators. *D. McIntosh. Trans. Roy. Soc. Canada* (2) 10, 41 (1904).—Sodium hydroxide and phenolphthaleine in alcohol become colorless when cooled to —80°, the color reappearing in case a large excess of alkali is added. When dissolved in liquefied halide acids or in liquefied ammonia, phenolphthaleine forms strongly-colored conducting solutions. The author finds it difficult to reconcile all the facts either with Ostwald's view of the color being due to the anion or with the chromophoric hypothesis. *W. D. B.*

Notes on Nernst filaments. *C. I. Zimmerman. Trans. Am. Electrochem. Soc.* 7, 79 (1905).—In addition to the electrolytic effect in a Nernst glower, there are other phenomena such as the conductivity of the air near the glower. If one lead of a voltameter is attached to the anode connection of a 200 volt D. C. glower and the free lead is used as an exploring wire to note the leakage

through the air, differences of potential of 50 volts can be detected. With electrostatic instruments and a 200 volt A. C. glower a deflection of 250 volts can be obtained. *W. D. B.*

Dielectricity and Optics

The specific inductive capacity of oleic acid and its salts. *L. Kahlenberg. Trans. Am. Electrochem. Soc., 7, 167 (1905).*—Pure anhydrous sodium oleate has a dielectric constant of 2.75 at 20°. Just above the melting-point the value is 2.8. Solid lead oleate gave a value of 3.27 at 18° and 3.70 when melted. The values for aluminum, ferric and copper oleates at 20° are 2.40, 2.68 and 2.80, respectively. At 20° oleic acid itself appears to have a dielectric constant lying between 2.50 and 2.60. A saturated solution of copper oleate in pyridine has a dielectric constant of 10.5 as against 12.5 for pure pyridine. *W. D. B.*

Electrical extraction of nitrogen from the air. *J. S. Edström. Trans. Am. Electrochem. Soc., 6, II, 17 (1904).*—In the Birkeland and Eyde process for making nitric acid, the arc is drawn out by a magnet and therefore moves forward and back along the electrodes, making a disc-shaped flame. The electrodes are not badly corroded and may be of copper or iron. It is claimed that 900 kg HNO_3 can be obtained per kilowatt-year expended in the arc.

W. D. B.

The production of negative ions from glowing metal compounds and related phenomena. *A. Wehnelt. Drude's Ann., 14, 425 (1904).*—A qualitative examination is made of the effect on the cathode fall of metal compounds in the glowing condition. A quantitative study is made of the influence of glowing metallic oxides under various conditions of pressure and temperature, and the use of hot oxides for the production of soft rays. Oxide-covered electrodes are studied. The paper is a very complete one and includes a careful discussion of previous work. The most striking result of the work seems to be the great influence which the metallic oxides have in reducing the cathode fall by the copious discharge of negative ions. *H. T. B.*

The mercury arc. *E. Weintraub. Trans. Am. Electrochem. Soc. 7, 273 (1905).*—A discussion of the properties and nature of the conductivity of metallic vapors. The current has to create the material which is to carry it from one electrode to the other, an arc discharge in metallic vapors being a discharge deriving its carriers, at least in the immediate neighborhood of the cathode, from the material of that cathode. The arc discharge is made possible if a spark or small arc is produced at the surface of the cathode. If the pressure of the ordinary mercury vapor volatilized from the cathode is kept down to a certain value, the conductivity of the arc is almost exactly proportional to the current and the voltage across the arc is therefore almost independent of the current.

While disintegration is characteristic of the cathode of a metallic arc in an exhausted space, the largest part of the loss of weight is due to mechanical disintegration. A transfer of matter either does not take place at all, or is so small as to be of the order of magnitude that would be required by the value of the electronic mass accepted in the modern theories. The cathode is the only place where the current-bearing material is formed.

The temperature of the cathode is not the cause of ionization in the case of metallic arcs in an exhausted space. The author looks upon an arc as a flow of negative electrons directed from the cathode towards the anode. *W. D. B.*

Arcs. *W. R. Whitney. Trans. Am. Electrochem Soc.*, 7, 291 (*1905*).—The best agreement between fact and experiment is obtained by postulating that an arc is due to the flow of negative ions from the cathode to the anode. Although the anode is the hotter of the two, it is always the cathode that is used up. The absolute loss of weight at the cathode varies very markedly with slight differences of composition but is always much less than equivalent to that which a copper anode would show in acidified copper sulphate solution. Copper as cathode of a sub-aqueous arc lost only five thousandths of the electrolytic equivalent. From the results on sub-aqueous arcs, "we may conclude that it seems necessary for arcs to lose material from the cathode during operation; that the anode need not change, though it may gain in weight; that the Faraday equivalent is not concerned in the process, and that the greater part, if not all, of the material leaving the cathode need not be deposited on or even reach the anode. If, then, this current is carried across the arc gap by particles of metal, it is most probably by negative particles, and during the process the excess of the material of the negative electrode is vaporized, even when this is a small wire surrounded by water. *W. D. B.*

The hot oxide coherer. *M. Bornemann. Drude's Ann.*, 14, *129* (*1904*).—It is found that heated iron or copper oxide in contact with lead gives a very sensitive coherer. The author considers that the influence of the electric waves is to reduce the thermoelectromotive force. *H. T. B.*

The cathode rays of radium. *F. Paschen. Drude's Ann.*, 14, *389* *1904*.—The author quite erroneously concludes from his experiments that the X-rays are cathode rays of high velocity and penetrating power. *H. T. B.*

The penetrating rays of radium. *F. Paschen. Drude's Ann.*, 14, *164* (*1904*).—The author brings forward tests to show that the X-rays from radium possess a negative charge. He considers it proved that the rays consist of negative particles moving with the velocity of light. He has since been shown to be entirely wrong, his negative charge being due to a secondary radiation set up on the surface by the infringing rays. *H. T. B.*

The spark spectrum of radium. *C. Runge and J. Precht. Drude's Ann.* 14, *418* (*1904*).—Having been supplied with a fresh quantity of pure radium bromide from Giesel the authors are enabled to extend their study of the spark spectrum particularly in the red end. They publish a table giving all observed lines together with photographs. *H. T. B.*

Sparking potential in chlorine, bromine and helium. *F. Ritter. Drude's Ann.*, 14, *118* (*1904*).—The theory of Orgler in regard to the division of the sparking potential in a gas is assumed. The ratio of the tension required to penetrate the gas to that required to penetrate air is obtained, giving what may be called a specific electric strength. This ratio for chlorine is found to be 1.78 and for bromine 1.98. No definite values could be obtained for helium. Warburg's spark retardation is less for helium than for air. *H. T. B.*

The action of canal rays on zinc oxide. II. *J. Tafel. Drude's Ann.*, 14, *206* (*1904*).—A reply to G. C. Schmidt's criticism (see review) of the author's theory to account for the action of the canal rays on aluminum and zinc oxide.

H. T. B.

The illumination of rarefied gases in the Tesla field. *K. Przibram. Drude's Ann.*, 14, *378* (*1904*).—Air, oxygen, carbon dioxide and hydrogen are used in electrodeless tubes subjected to a rapidly alternating electric field. *H. T. B.*

The origin of the electric gas spectra. *J. Stark. Drude's Ann.*, 14, *506* (*1904*).—The author develops a theory to account for gas spectra on the basis that the acceleration of an electron is conditioned by joining with an atom or molecule, or, when free, by collisions. Whether caused by temperature or an electric field a change in velocity produces the same effect. An idea of electric temperature is introduced when the change is brought about by the electric field. It is supposed that line spectra are due to atoms which have lost one or more electrons and that band spectra are due to the combination of a negative electron with the positive ions. A comparison of chemical elements is made with regard to their power of supplying the line and band spectrum.

H. T. B.

The relative intensity of the spectra of mixed gases. *E. Waetzmann. Drude's Ann.*, 14, *772* (*1904*).—This is an experimental determination of the intensities of the lines of the hydrogen spectrum with mixtures of nitrogen. It is found that small admixtures cause a decrease in the spectrum of a pure gas.

H. T. B.

The dependence of the photometric brilliancy on the temperature of glowing bodies. *E. Rasch. Drude's Ann.*, 14, *193* (*1904*).—The present paper is of use to those interested in optical pyrometry. The relation between brilliancy and temperature as expressed in various equations is discussed at some length. It is found that the simple expression of Lummer and Pringsheim does not give the best results, while the equation of LeChatelier and Boudouard is more nearly correct. The melting-point of iridium is computed to be 2287° C.

H. T. B.

The influence of illumination on the use of the wedge compensation saccharimeter. *O. Schönrock. Drude's Ann.*, 14, *406* (*1905*).—After defining carefully the hundred point on the Ventzke scale, the effects of different sorts of light are tried on the rotation of the quartz plate. The effect of temperature on the rotation is also tried and it is found to exert a large influence. The rotation is studied for mixed lights and for different observers, and a contrast is made between mixed and homogeneous light. *H. T. B.*

An optical method for observing the diffusion in electrolytes. *C. Hambuechen. Trans. Am. Electrochem. Soc.*, 7, *305* (*1905*).—If an electrolytic cell with plane sides be placed in a projection lantern, differences of density can be recognized which cannot be detected by the unaided eye. The author recommends this as a means for determining the suitable arrangement of baffle plates; but if this were to be done special precautions would have to be taken to guard against temperature changes due to the heat from the lantern. *W. D. B.*

The optical properties of developed Lippmann emulsions. *R. E. Liesegang. Drude's Ann.*, 14, *630* (*1904*).—The author studies the colors of the films formed in developing Lippmann plates, and attributes them to the molecular complexity of the silver. *H. T. B.*

Artificial double refraction and elasticity of gelatine plates. *A. Leick. Drude's Ann.*, 14, *139* (*1904*).—It is shown that the specific double refraction of pure water gelatine solutions is proportional to the concentration and that the modulus of elasticity is nearly proportional to the square of the concentration. The presence of different salts lowers the double refraction, tension and modulus of elasticity. Glycerine and cane sugar lower the double refraction but raise the modulus of elasticity. *H. T. B.*

Double refraction in jellies by swelling and shrinking. *G. Quincke. Drude's Ann.*, 14, *849*; 15, *1* (*1904*).—A continuation of the author's previous work, in which the existence of foam cells with liquid or solid foam walls in jellies is treated of, and the investigation carried out with respect to their property of double refraction. Interesting diagrams are given. *H. T. B.*

Crystallography, Capillarity and Viscosity

Forced oscillations in polarized mercury drops. *P. G. Gundry. Drude's Ann.*, 14, *590* (*1904*).—The author adopts the method of drop oscillation developed by Rayleigh and Lenard for the determination of the surface tension of mercury in electrolytes. The experimental part is very nicely described and makes a pretty piece of research. The drops are made to oscillate in resonance with the discharge from a small induction coil. Photographs are obtained and reproduced of the fundamental and harmonic oscillations. In dilute sulphuric acid the value of the surface tension of mercury comes 264 dynes per centimeter as against Paschen's value which is 312. *H. T B.*

On the force of extension. *G. Quincke. Drude's Ann.*, 15, *55* (*1904*).—The present paper is a justification of the author's position in regard to changes shown in surface layers, of which he has made such a study. The work of van der Mensbrugghe is specially discussed. *H. T. B.*

The viscosity and temperature coefficient of oxygen, hydrogen, chemically prepared and atmospheric nitrogen. *H. Markowski. Drude's Ann.*, 14, *742* (*1904*).—It is shown that the viscosity of oxygen, hydrogen and nitrogen between 0° and 183° C is well represented by Sutherland's formula. With the exception of hydrogen, the temperature coefficient decreases with increasing temperature above 0°. From the kinetic theory of gases the author calculates the path and collisions of the molecules. *H. T. B.*

Remark to the paper by Markowski on the internal friction of oxygen, hydrogen, and nitrogen. *A. Bestelmeyer. Drude's Ann.*, 15, *423* (*1904*).—A reply to Markowski who claims to have observed a difference in the internal friction of atmospheric nitrogen as compared to that produced chemically. The author shows that the differences observed are within the limits of experimental error. *H. T. B.*

ON THE NATURE OF THE PROCESS OF OSMOSIS AND OSMOTIC PRESSURE WITH OBSERVATIONS CONCERNING DIALYSIS[1]

BY LOUIS KAHLENBERG

Introduction

A brief but excellent outline of the history of the development of our knowledge of osmosis up to 1877 is given by Pfeffer in his well-known monograph, "Osmotische Untersuchungen." The great importance of osmotic phenomena in physiological processes was clearly recognized as early as 1826 by Dutrochet, and for half a century later osmotic investigations were conducted very largely, though not exclusively, in the interests of physiology. Precipitated membranes were first used by the botanist, Moritz Traube,[2] in 1865, and these were employed by Pfeffer in his researches above mentioned. Special interest in osmosis has developed since 1887, when by using Pfeffer's data of osmotic pressure measurements van't Hoff sought to show that the simple gas laws hold for dilute solutions. Since the latter date so-called semipermeable membranes have been used almost exclusively in osmotic investigations. These membranes usually consisted of ferrocyanide precipitates of some heavy metal, copper ferrocyanide being the favorite precipitate for osmotic work, though the ferrocyanides of zinc and nickel were occasionally employed, as were also a few other precipitates.

In this later work effort in two directions is clearly discernible: (1) Those who have been favorable to van't Hoff's hypothesis of solutions (based on the analogy between gases and solutions), according to which the osmotic pressure, so-called, is due to the bombardment of the semipermeable membrane by the dissolved molecules, have sought either to compare osmotic pressures of aqueous solutions with each other, or to measure directly the osmotic pressure of certain solutions in the hope of securing data to uphold the theory. It is

[1] Published also in the Transactions of the Wisconsin Academy of Sciences, Arts and Letters, Vol. 15, Part I.

[2] Centralblatt f. medic. Wissenschaften, 1865.

true, however, that considering the vast importance of direct measurements of osmotic pressure for the van't Hoff theory of solutions, but little effort has been made to measure osmotic pressures directly. This has come about very largely because of the attitude taken in the matter by the main adherents of the van't Hoff theory who voiced and continually supported the dogma that the osmotic pressure is necessarily independent of the nature of the membrane if it be semipermeable; and that since it is very difficult to measure osmotic pressures directly, it is better to content one's self with the so-called "indirect" measurements of osmotic pressure, namely, with a computation of the latter from vapor tension, freezing-point or boiling-point observations on solutions, which, be it remembered, involve the assumption that the gas laws hold for solutions. And so we have the rather remarkable situation that direct measurements of osmotic pressure, and indeed the general investigation of osmosis, has not only been neglected by the chief advocates of the gas theory of solutions, but they have in addition actually discouraged work in this direction through the attitude they have taken. They have even claimed to have proven by thermodynamics that the osmotic pressure must be independent of the nature of the membrane provided the latter is semipermeable. The assumptions made in such "proofs," and the fact that there is in reality no such thing as a semipermeable membrane in the strict sense of the word, have been passed over lightly. (2) Quite a different direction in the investigation of osmotic phenomena has been taken by those who have held van't Hoff's conception of the nature of osmotic pressure to be untenable. These men have continually brought forward experiments, of a qualitative nature to be sure, showing that the hypothesis of van't Hoff cannot be held and that no special stress is to be laid upon direct measurements of osmotic pressure, which they have consequently not attempted to make.

In his efforts to measure osmotic pressures directly,

Tammann[1] came to the conclusion that it is not possible to obtain reliable, concordant results by means of the method adopted by Pfeffer,[2] which he consequently abandoned entirely and turned his attention to comparing the osmotic activity of various solutions with one another. Attempts at direct measurements of osmotic pressure have again been taken up recently by H. N. Morse[3] and his coworkers. They have measured the osmotic pressures that are developed when aqueous sugar solutions are separated from water by means of precipitated membranes of copper ferrocyanide. The method they employed is essentially that of Pfeffer, with the exception that they prepared the membranes with the aid of electrolysis. Enough can hardly be said in praise of the care and perseverance exercised by Morse and his assistants in this work, and yet they have neglected a very essential point in their determinations as will appear from considerations given below, and consequently their experiments are not conclusive in establishing, as they suppose, that the gas laws hold fairly well for the osmotic pressures of aqueous sugar solutions, using copper ferrocyanide membranes. Furthermore, attempts to generalize from the data collected by Morse and Frazer on aqueous sugar solutions, as to the behavior of all solutions taking no consideration of the membranes employed, are quite unwarranted. Moreover, while according to Morse and Frazer and also according to Flusin[4] the aqueous sugar solutions show osmotic pressures in approximate conformity to the gas laws, the Earl of Berkeley and E. G. J. Hartley[5] have found materially higher pressures than those deduced from the gas law, even though their membranes,

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[1] Wied. Ann., 34, 299 (1888). See later attempts by new method, Zeit. phys. Chem., 9, 97 (1892).

[2] Pfeffer, be it remembered, worked solely in the interests of physiology and for his special purpose his experiments were quite sufficient.

[3] Am. Chem. Jour., 34, 1 (1905).

[4] Comptes rendus, 132, 1110 (1901).

[5] Proc. Roy. Soc., 73, 436 (1904).

which were also prepared with the aid of electrolysis, were admittedly not perfectly tight.

Among the many opponents of the van't Hoff theory of osmosis may be mentioned Lothar Meyer, Raoult, Fitzgerald, Pickering, Quincke, Dieterici, J. Traube, Battelli and Stephanini. The opponents of the van't Hoff idea have generally held that the so-called osmotic pressure is an ordinary hydrostatic pressure brought about by entrance of liquid into the osmotic cell. Concerning the reason for this entrance of additional liquid into the osmotic cell there has, however, been difference of opinion; some holding that it is due to attraction that is essentially chemical in character; others that it is due to capillarity; and still others that it is caused by surface tension. The latter view has lately been prominently brought forth by Traube,[1] whose claim is that "the difference in surface tensions determines the direction and velocity of the osmosis." His idea is that the main direction of osmosis is always toward the liquid having the greater surface tension. Again, Battelli and Stephanini[2] also express the opinion that difference in surface tension is the cause of osmosis. But on the basis of their experimental work, they modify Traube's contention to the effect that the main osmotic current is not always toward the liquid of higher surface tension, but that the process always proceeds in such a direction as to tend to equalize the surface tensions of the liquids on the opposite sides of the septum. Very recently Barlow[3] has also brought forward cases which are not in harmony with the theory of Traube.

In the present investigation the main purpose has been to inquire into the nature of osmosis and osmotic pressure, and to test whether the latter really follows the gas laws. To this end a considerable number of osmotic experiments were performed in which liquids of similar and also of very different

[1] Phil. Mag. [6], 8, 704 (1904).
[2] Atti della Reale Accademia dei Lincei, 14, 3 (1905).
[3] Phil. Mag. [6], 10, 1 (1905).

character were separated from each other by different membranes. In this work observations were taken as to the direction of osmosis with change of membrane, with change of solvent and also with change of solute. The effect of temperature was considered. The degree of permeability of the membranes for various substances was noted, with the result that membranes as semipermeable as any known hitherto were found, which are yet not precipitated membranes. Furthermore it was ascertained *why* the membranes were semipermeable in some cases and not in others. It was consequently possible to foretell for which substances the membranes were permeable and for which substances not permeable. Further, this work has cast light on the process of dialysis. It has been possible to separate different dissolved crystalline substances from each other by dialysis, and also to separate dissolved crystalline from non-crystalline bodies by having the *non-crystalline substances pass through the septum* and the crystalline ones remain behind in solution in the dialyzer. The direct measurements made with the semipermeable membranes employed, moreover, showed that the gas laws do not hold at all in these cases. It was also found that in making direct measurements of osmotic pressures it is necessary to *stir* the liquids separated by the membrane, a very important fact which has been entirely overlooked in all osmotic pressure determinations hitherto made. The necessity of such stirring was really discovered accidentally, as will appear from details given below, after having worked in vain for over a year trying to get reliable, concordant results without stirring. The discovery that agitation of the liquids is essential in osmotic pressure measurements is of paramount importance in deciding as to the nature of the osmotic process.

In the presentation of the experimental work which now follows, the experiments will not be described in the order in which they were actually performed for the reason that greater clearness will be obtained by detailing the results in the light

of the theory which was gradually evolved in the course of the investigation.

A Typical Case of Osmosis

If chloroform A, Fig. 1, be placed in a glass tube and a layer of water B be poured upon it, and again a layer of ether C be carefully poured upon the water, and the whole be allowed to stand, there will eventually be but two layers A′ and B′, Fig. 2. An examination of A′ shows that it consists of chloroform and ether saturated with water, whereas the layer B′ consists of water saturated with ether and chloroform. In the change which has taken place, one layer, that of the ether, has gradually disappeared, and the lower layer has greatly increased in bulk and lifted the aqueous layer to the top. The explanation of this phenomenon is evident. Ether dissolves very readily in chloroform, but in water it dissolves much less readily; again, chloroform and water hardly dissolve each other at all. In the arrangement we have in Fig. 1, the aqueous layer B dissolves ether, and in turn the ethereal layer C takes up some water. When the ether has gone into B until it touches the chloroform layer A, the latter extracts ether from the aqueous layer B. Thus the upper part of the chloroform layer A becomes enriched with ether, whereas

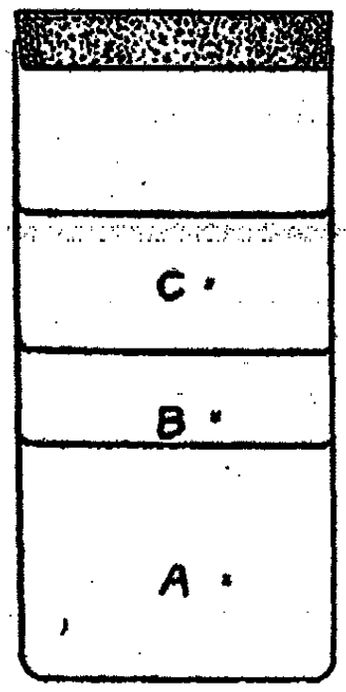


Fig. 1

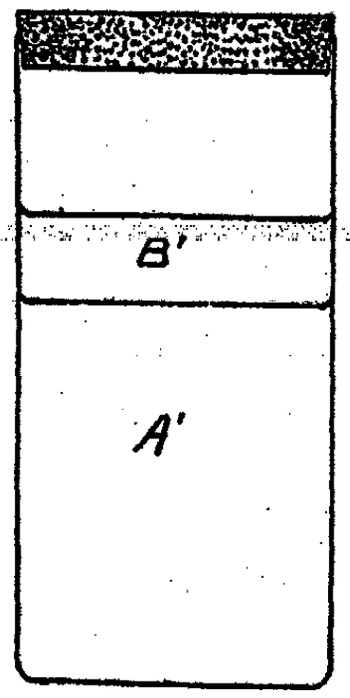


Fig. 2

the lower part of the aqueous layer B becomes depleted in ether. The latter depletion is made good by a continuous supply of ether from the upper parts of B, which are in turn supplied with ether from C. Again, the ether in the upper layers of A gradually diffuses into the more distant parts of A. This process of the transportation of the ether in C through B into A proceeds, then, until the supply in C is exhausted. It is to be noted, however, that since chloroform is more soluble in water containing ether than in pure water, the aqueous layer B will take up more chloroform after becoming charged with ether. Thus some of the chloroform is making its way upward into the aqueous layer B, from which it also passes in part into the ethereal layer C.

It is clear then that the ether of layer C is making its way through the aqueous layer B into the chloroform layer A, and that on the other hand the chloroform is passing into the aqueous layer B charged with ether and further into C. Thus we have currents of ether and chloroform going in opposite directions. The movement of the chloroform as to quantity is, however, extremely slight as compared with that of the ether; and so the movement of the latter practically predominates and the ethereal layer is finally absorbed. It must be borne in mind, however, that water, being somewhat more soluble in chloroform charged with ether than in pure chloroform, will to a slight extent go into the layer A as it becomes enriched with ether; and, as has already been remarked, some water also passes into the layer C, for water is somewhat soluble in ether. When the change is complete, we have, as stated above, a lower layer consisting of chloroform and ether saturated with water, and an upper layer of water saturated with ether and chloroform.

The rate at which this process goes on depends on the temperature and upon the pressure, but also upon the thickness of the aqueous layer B and the area of the surface of contact with the ethereal layer C and the chloroform layer A. It is further clear that the process would be hastened if each

of the layers A, B, and C were continually stirred, for by so doing the slow processes of diffusion would be aided and the changes in concentration which take place in the layers where they are in contact with one another would be lessened.

Summed up then, the observed change goes on because ether is soluble in water, but much more readily soluble in chloroform, so that the latter is able to extract ether from the aqueous solution of ether, B. The chloroform-ether solution in A may be regarded as a solution of chloroform in ether, especially after a considerable quantity of ether has accumulated in it; and since but very little chloroform passes into the aqueous layer B, the latter is practically permeable only for ether, and therefore this aqueous layer B acts as a *semipermeable septum*. It permits ether to pass from C to A, but allows very little, practically no, chloroform to pass into C. It is clear further that as A becomes richer and richer in ether, the tendency for more ether to enter A from B becomes less and less. Ether dissolves more readily in chloroform than in water because ether and chloroform have a greater mutual attraction for each other than have ether and water; it is for this reason too that chloroform is able to extract ether from an aqueous solution of the latter. As ether accumulates in A, however, the power of this layer to extract ether from the aqueous layer B diminishes, because the attraction or affinity of chloroform and ether for each other becomes more and more satisfied. Finally, suppose we prevent the supply of ether in C from becoming exhausted by adding some as may be required, a point will be reached where compartment A has become so rich in ether that the attraction or affinity of this chloroform-ether solution for additional ether has decreased to such an extent that it can no longer extract further ether from the aqueous layer B. In other words, when the chloroform solution in ether, A, has become so dilute that its attraction for additional ether just equals the attraction of water for ether in the aqueous layer B, the process is arrested. The point at which this occurs would clearly vary with the temperature and also with the pressure.

If in Fig. 1 compartment A be filled with carbon bisulphide instead of chloroform, the process would go on as before in a similar manner and for perfectly similar reasons. Indeed, any liquid which in itself does not mix with water, practically speaking, and yet has a greater attraction for ether than has water, would serve in place of the chloroform. The rapidity with which the process proceeds and the final point of equilibrium reached would, however, also be a function of the nature of the substance so employed. If in Fig. 1 the ether in C be replaced by an oil, say olive oil or a hydrocarbon oil, retaining the water in B and chloroform in A, nothing will take place,[1] for these oils are not appreciably soluble in water, that is to say, the attraction or affinity existing between them and water is insufficient to overcome their cohesions to the extent necessary to cause a fusion, a blending, an interpenetration of their masses. Again, if the water in B were replaced by a liquid in which neither ether nor chloroform are appreciably soluble, nothing would take place. Further, if the chloroform A be replaced by a liquid which does not dissolve water and has less attraction for ether than has water, nothing will take place. *It is clear then that the process under consideration proceeds because of the specific nature of the septum B and also that of the two liquids that bathe it.* It should also be emphasized in this connection that while it is essential, as stated above, that the layer B, the water, must be capable of dissolving C, the ether, it is further necessary that this solubility be restricted in character, as it is in fact, otherwise the layer B would not be distinct from C and would become so rich in ether that the boundary lines between A and B would also disappear.

[1] If olive oil be dissolved in ether and this solution placed in C, whereas water and chloroform are retained in B and A, respectively, the ether would pass through the water into the chloroform, leaving the olive oil behind in C. We have here an illustration of what may be called selective action on part of the membrane (the aqueous septum B) in which property biologists are particularly interested. The explanation is obvious. Water dissolves ether appreciably, but not olive oil, so the latter is left behind.

Returning now to the original experiment Fig. 1 in which ether, water and chloroform are in A, B, and C respectively, let us imagine the aqueous layer B as quasi-solid and also immovable, *i. e.*, attached firmly to the sides of the glass tube, nevertheless otherwise retaining its original properties. This would make A a compartment whose volume remains fixed, and as the ether enters it from B, for reasons already detailed, a hydrostatic pressure would be produced upon the sides, top and bottom of A; and as this pressure develops, it would become more and more difficult for additional ether to enter this compartment. Finally if the walls of this compartment did not give way, a point of maximum pressure would be reached. At this point, at the temperature of the experiment, the affinity of the ether-chloroform solution in A for additional ether is insufficient to extract further ether from the aqueous layer B. In other words, the affinity of water for ether aided by the hydrostatic pressure developed in A (which militates against the ether passing into A) just balances the affinity of the chloroform-ether solution in A for additional ether. And yet the case is after all not quite so simple, for it must be remembered that chloroform is somewhat soluble in water saturated with ether at atmospheric pressure; now this solubility is increased with increase of pressure, so that as the hydrostatic pressure in compartment A increases due to the influx of ether, the outflow of chloroform is continually slightly increasing, which tends, of course, to relieve the pressure. The actual final maximum pressure reached is therefore determined by the relative influx of ether into compartment A and the outflow of chloroform from that compartment. When this outflow is practically nil, or at any rate very slight, we should be dealing with a so-called semipermeable membrane; when the outflow is not a negligible quantity, as in the case of most septa, the final maximum pressure attained is materially influenced thereby.

Now it is easy enough to imagine the aqueous layer B firmly held in place as we have done, but to realize this ex-

perimentally presents great difficulties. It may, however, readily be demonstrated that such hydrostatic pressure is actually produced, without, to be sure, making an attempt to furnish anything more than a qualitative proof that such pressure is really formed. The apparatus used for this purpose is shown in Fig. 3. In this glass tube, D represents mercury, A chloro-

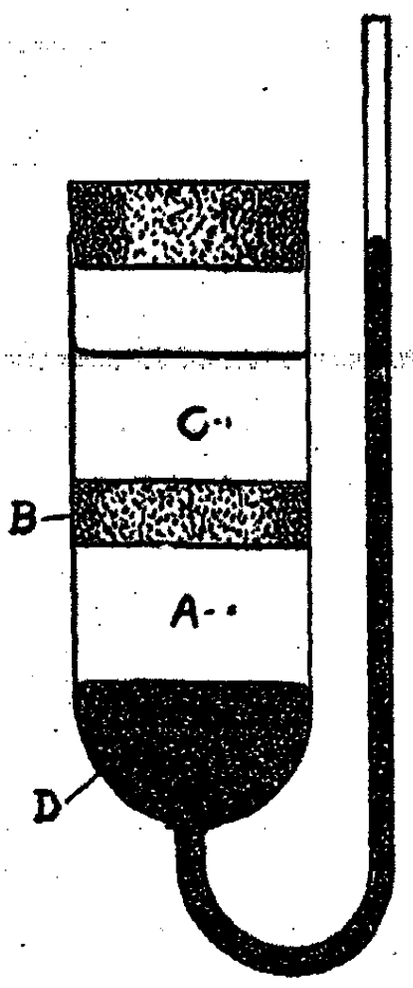


Fig. 3

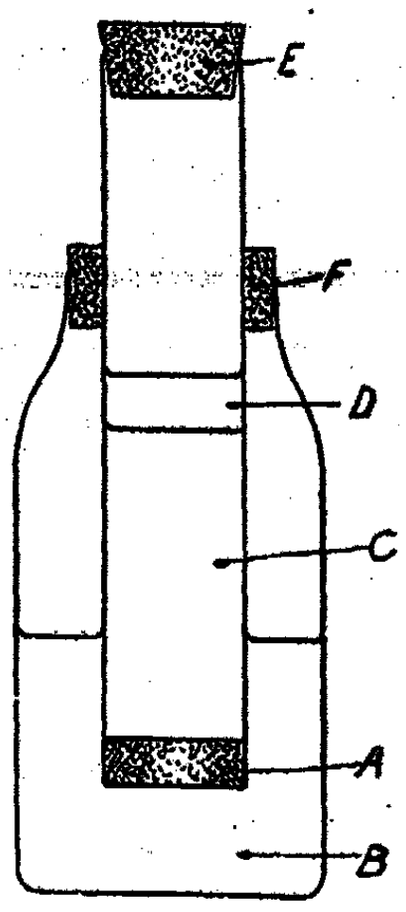


Fig. 4.

form, C ether, and B is a slice of an excellent piece of cork which had been kept under boiling water for some time so as to drive the air out of it and thoroughly inject it with water; during this process much soluble material was also extracted from the cork. The cork thus thoroughly soaked with water was firmly pushed into position. It is of course somewhat difficult to avoid having air bubbles just above and below the cork, but by careful manipulation it is possible to secure the arrangement as shown in Fig. 3. The chloroform and ether used in this case were each first saturated with water, so that they would not unduly rob the cork of its water content,

which was necessarily small enough to begin with. On allowing the apparatus to stand, the mercury rises in the tube as indicated, showing that pressure is produced on the walls of A. The mercury rose until the cork either broke or began to slip upward, the experiment being repeated three times. Using a cork not soaked in water no pressure was obtained. It is quite probable that a cork might be so fastened in place by the aid of mechanical contrivances that an ordinary tube would give way before the cork would move; but since the maximum pressure could not be measured in this manner, the qualitative demonstration of the presence of the pressure was deemed sufficient. The experiment just described may be performed also in the form illustrated in Fig. 4, which is more like the usual arrangement employed in osmotic experiments. In this figure, the liquid B in the bottom of the bottle is ether; the end of the glass tube is closed with a tight-fitting slice of cork A saturated with water; in the tube above the cork is chloroform C; and above the chloroform is water D. At F there is a cork collar which holds the tube in place. This collar does not fit perfectly tight, yet it minimizes the evaporation of the ether. The cork E is rather loosely inserted; its purpose is simply to prevent undue evaporation. This was also the purpose of the layer of water D, which, to be sure, also kept the chloroform saturated with water. Both the ether and chloroform used were saturated with water to begin with as in the previous case. With this arrangement the layer C increased in bulk, the column rising until the layer D touched the cork E. The experiment was continued for two weeks; the cork at A being rather thick caused the change to progress slowly.[1]

This case of ether, water, chloroform (Fig. 1) has been thus described in detail because it illustrates all the essential points to be taken into consideration in the study of the osmotic process. We have seen what conditions are necessary for the

[1] Compare in this connection a similar experiment of Nernst: Zeit. phys. Chem., 6, 35 (1890).

process to proceed at all, what are the various factors that modify the rate of the change, and what causes the so-called osmotic pressure. It has further been shown under what conditions we get a so-called semipermeable membrane, and it is evident that an absolutely semipermeable membrane exists only in theory. On the basis of his elaborate experimental researches, Quincke[1] has also arrived at this conclusion. He stoutly contends that there really is no such a thing as a semipermeable membrane and that a theory which postulates such cannot be maintained. His words are, "Ich bestreite, dass eine halbdurchlässige Membran existirt. Damit fällt aber auch der osmotische Druck, dessen Theorie die Existenz einer halbdurchlässigen Membran voraussetzt." As stated above, there is in general always an outflow from an osmotic cell as well as an inflow, and when the former is extremely slight as compared with the latter, the membrane is *called* semipermeable; but commonly the outflow is quite sufficient to demand consideration. At any rate, the osmotic pressure is always the resultant of inflow and outflow caused by the attractions that come into play, which attractions are to the mind of the writer the same as what is commonly called chemical affinity, and consequently such so-called osmotic pressures may, under suitable conditions, be very great indeed, while under other conditions they may be quite small. They would, moreover, present considerable variation according to the nature of the substances employed.

No originality is claimed for the ether, water, chloroform experiment, Fig. 1. It occurred to me after a goodly number of the experiments described below had been performed; but in looking over the earlier articles of the rather voluminous literature on the subject of osmosis, I found that in 1854 L'Hermite[2] described the experiment in question. His statements concerning its import and bearing are very clear, though of course he does not speak of semipermeable mem-

[1] Drude's Ann., 7, 682 (1902).

[2] Comptes rendus, 39, 1177 (1854).

branes and osmotic pressures, for these concepts were at that time quite unknown. A reference to the article of L'Hermite is also made in the bibliography in Lehmann's Molekularphysik.

However, after having L'Hermite's experiment clearly before me, the principles it illustrates soon became the guide in future experimentation, for they enabled me to foretell whether a membrane would be permeable or impermeable for a certain substance under given conditions; and if permeable for several substances, which of these would go through most readily. I was thus enabled to forecast in which direction the main osmotic current would go. These matters were not only of consequence in direct measurements of osmotic pressures, detailed below, but they were also of importance in dialysis as will appear farther on. Again, by demonstrating the nature of the process, it clearly appeared that in determining the maximum osmotic pressure the contents of the osmotic cell must be continually stirred. For, taking the arrangement as given in Fig. 1 and again imagining the aqueous layer B as quasi solid and firmly fixed in place, it is evident that as ether is drawn into compartment A, the liquid in that compartment becomes enriched with ether just where it touches B, and that consequently the osmotic pressure set up in A is not as great as it would be if the liquid in A were continually stirred so as to rapidly distribute the incoming ether throughout the cell and present a fresh surface to the layer B. When stirring is omitted, this work of keeping the contents of B of uniform concentration has to be performed by diffusion, a process which is very slow, and consequently a lower pressure is obtained. It is clear that for similar reasons the contents of B ought in general also to be stirred in attempting to measure the maximum osmotic pressure, as should also the liquid C. But when B is quite thin, as is the case with some membranes, stirring its contents is of less consequence. Furthermore, when practically very little of A enters C (*i. e.*, when B is a so-called semiper-

meable septum) it is obviously not so necessary to stir the contents of C in osmotic pressure measurements. But the liquid in the osmotic cell must *always* be stirred, though it is recognized that in some forms of cells this is far more imperative than in others. Attempts to make direct measurements of osmotic pressures without stirring the contents of the cell are comparable with attempts to make a saturated solution of a salt by placing an excess of it in a dish, pouring the solvent upon it and allowing the whole to stand without agitation. The method of stirring the contents of the osmotic cell will be described below in connection with the quantitative measurements of osmotic pressures.

Qualitative Experiments

The following experiments which are largely of a qualitative nature were performed in the course of the investigation in order to determine the influence which the character of the membrane has upon the permeability of the latter, and also upon the main direction of the osmotic current. Unless otherwise stated, the osmometer used was a very simple one, consisting of an ordinary thistle tube, the mouth of which was closed with the membrane employed. The latter was tied on with thread, in which process great care was used to secure a perfect contact between the glass and the membrane. To accomplish this a thistle tube was selected with a flare of about 45° at the mouth. On such a tube the membranes used could be perfectly securely tied. Very many evenly applied turns of a stout, moderately fine, white cotton thread were wound on after the membrane had been carefully placed in position over the mouth of the tube. This part of the work required much time, patience and perseverance, as well as skill and practice. After thus securing the membrane over the mouth of the thistle tube, the latter was filled with one of the liquids to a point slightly above the bell of the tube, which was then immersed in a beaker containing the other liquid. The level of the two liquids was, of course, the same to begin with.

For convenience in future reference the experiments performed have been numbered. The liquid in the bell of the osmometer will always be called the inner or inside liquid; that in the beaker, the outer or outside liquid.

1. The membrane consisted of sheet rubber, vulcanized caoutchouc, such as is used by dentists in making their "rubber dam." This rubber was very elastic, being almost the pure gum. It could readily be stretched over the osmometer and tied on so as to form a perfect joint, for all folds could be avoided. The inside liquid was a 20 percent aqueous cane sugar solution; the outside liquid was pure water. The experiment ran forty-eight hours. No change took place. The liquids remained at the same level and no sugar passed through the membrane into the water on the outside.

2. A rubber membrane was used as before. The inside liquid consisted of a 20 percent aqueous NaCl solution, the outside liquid of pure water. No change took place, the liquids remaining on the same level and not a trace of salt appearing in the water without. When the outside water was replaced with toluene, the latter caused the rubber to swell, but no salt or water passed into the toluene, neither did the toluene go into the brine. On afterward exposing the membrane to the air, it lost its toluene content and shrank to its former size, remaining throughout quite elastic.

Experiments 1 and 2 show that it is possible to get the joint between rubber and glass perfectly tight. It is perfectly clear that no change took place when water and the aqueous solutions touched the rubber, for the reason that there is no affinity between these liquids and rubber. Thus the first condition necessary for osmosis to take place was lacking, namely, that the membrane must be able to dissolve (*i. e.*, imbibe or take up) one of the liquids that bathe it. When in the second part of experiment 2 the water was replaced by toluene, the latter was taken up by the membrane; but osmosis did not take place because the liquid on the other side, the brine, having no affinity for toluene to speak of was unable to extract toluene from the rubber.

3. The inside liquid was water, the outside liquid 99.5 percent alcohol, the membrane rubber. The liquid rose in the osmometer, showing the main current to be from the alcohol through the rubber to the water. This is what one would expect, for the alcohol is taken up by the rubber and then the water by virtue of its affinity for alcohol extracts the latter from the rubber.

4. This experiment was like No. 3 except that a 20 percent aqueous cane sugar solution was used as the inner liquid. Again the liquid rose in the osmometer, alcohol passing through the rubber into the sugar solution. No sugar, however, was found in the alcohol on the outside. The rise in the osmometer tube was slow, being about 5 cm in five days. The inside diameter of the stem of the thistle tube was about 3.5 mm. The main direction of the current was, of course, such as was to have been expected from what was said in connection with the preceding experiment. No sugar was found in the alcohol outside, for sugar has so little affinity for alcohol, for rubber and for rubber soaked with alcohol that it is not taken up by any of these.

5. The inner liquid was pyridine, the outer liquid water and the membrane parchment. The liquid rose in the osmometer showing the main current to be from the water through the parchment to the pyridine. Some pyridine was also found in the water.

6. The experiment was like No. 5, except that a rubber membrane was used instead of parchment and the water was the inner liquid and the pyridine the outer. The liquid again rose in the osmometer, showing that the main current was in the opposite direction as in the preceding experiment, namely from the pyridine through the rubber to the water. Some water also passed into the pyridine, showing an appreciable minor current.

7. The inside liquid was pyridine, the outside liquid toluene and the membrane parchment. No change took place.

8. This experiment was like No. 7 except that rubber was substituted for parchment. The liquid at once rose in the osmometer, showing the main current to be from the toluene through the rubber to the pyridine. Some pyridine, however, also passed into the toluene.

Rubber readily takes up pyridine, and imbibes toluene still more readily; on the other hand, parchment does not, showing that it has but little affinity for these liquids. It is consequently easy to see why no change occurred in No. 7. When it is further remembered that pyridine and water are consolute liquids, as are also toluene and pyridine, the observations in Nos. 5, 6 and 8 are easily explained. In No. 5 the parchment imbibes water which is then extracted by the pyridine; but since pyridine is soluble in water-soaked parchment, some pyridine also passes into the water outside. In No. 6 the rubber imbibes the pyridine which is then extracted by the water; but as water is somewhat soluble in pyridine-soaked rubber, some of it makes its way into the pyridine without. In No. 8 the fact that toluene is imbibed more readily by rubber than is pyridine again determines the direction of the main current, though in this case, owing to the fact that pyridine has considerable affinity for rubber as well as for toluene, the minor current is of considerable consequence. The cases just considered well illustrate how the nature of the septum and of the liquids that bathe it determines what will actually take place.

In 1898, G. Flusin[1] used carbon disulphide, chloroform, toluene, ether, benzene, xylene, petroleum ether, benzyl chloride, turpentine, petroleum, nitrobenzene, methyl alcohol, ethyl alcohol, and acetic acid, taking these liquids in all possible combinations in pairs and separating them from each other by means of a membrane of vulcanized caoutchouc. He found the main current to be from the liquid which is the more readily imbibed by the rubber, through the septum to the less readily imbibed liquid. Again in 1900[1] he used water,

[1] Comptes rendus, 126, 1497 (1898); 131, 1308 (1900).

methyl alcohol, amyl alcohol, amyl acetate, chloroform, benzene, ether, and ethyl alcohol. He employed hog's bladder as a septum, placing one side of it in contact with ethyl alcohol (the liquid which of those named is, according to him, imbibed least readily) and bathing the other side with each of the other liquids successively. He always found the main current to be in the direction toward the ethyl alcohol and the rate of flow to vary with the amounts of liquid imbibed by the membrane during the first five minutes, which amounts, of course, were determined by independent experiments. I have confirmed all of the results of Flusin where he used rubber membranes. He says nothing, however, about the minor current, which I found to be present in all of these cases to a greater or lesser extent. In other words, the rubber was traversed by both liquids of each pair, though the main direction of the current was quite correctly determined. Flusin shows that the affinity between membrane and liquid is to be measured by the rate with which the latter is imbibed by the former, and not by the total amount of liquid taken up by a given quantity of membrane at the end of a long time, as Tammann[1] contends. Raoult[2] separated methyl alcohol and ether from each other by means of rubber. He always found the direction of the main current to be from the ether through the rubber to the methyl alcohol; and the direction of the main current remained the same, even when the ether was considerably diluted with methyl alcohol. When he substituted a membrane of hog's bladder for the rubber, the direction of the main current was reversed, it being from the methyl alcohol through the septum to the ether. In his article, Raoult has omitted to say anything about the fact that in his experiments there is also a minor current in a direction opposite to that of the major; in other words, that when caoutchouc is the membrane and ether is going into the alcohol there is also some alcohol passing into the ether, and

[1] Zeit. phys. Chem., 22, 491 (1897).

[2] Comptes Rendus, 21, 187 (1895); Zeit. phys. Chem., 17, 737 (1895).

when the bladder is employed there is some ether passing into the alcohol though the main current is that of the alcohol toward the ether. Raoult was, however, perfectly clear in his own mind with regard to this matter as will appear from a quotation from a letter written by him printed below.

It is hardly necessary to add that in the light of what has already been said above, the results obtained by Raoult and Flusin are exactly such as might have been foreseen.[1]

9. The inner liquid was glacial acetic acid, the outer liquid distilled water and the membrane rubber. Within five minutes blue litmus paper placed in the water turned red, showing that the acid was passing through the rubber. This was the direction of the main current, which might have been expected, since glacial acetic acid is more readily absorbed by rubber than is water.

10. The inner liquid was a 10 percent solution of acetic acid in water, the outer liquid water, and the membrane rubber. After one and a half hours the blue litmus in the water began to turn red, indicating that in this case too the acid was passing through the rubber into the water. The direction of the main current then was not altered by diluting the acetic acid considerably with water, which result is in line with what Raoult found in the ether—methyl alcohol experiment referred to above.

11. The inner liquid was a strong solution of trichloracetic acid in water, the outer liquid water and the septum rubber. But very little acid passed through the rubber into the water. Hardly any change took place in the twenty hours, during which the experiment was continued.

12. The inside liquid was a solution of trichloracetic acid in benzene, the outside liquid water and the membrane rubber. In this case acid went into the water in very considerable quantity. This was the direction of the main current. The experiment was run for twenty hours.

13. The inner liquid was a solution of trichloracetic acid

[1] Compare also remarks by Tammann: Zeit. phys. Chem., 22, 490 (1897).

in water to which considerable benzene had been added, the outer liquid was water and the septum rubber. Very notable quantities of acid passed through the membrane into the water without. The experiment was continued for twenty hours.

The large increase in the amount of trichloracetic acid which passed through the rubber in 12 as compared with 11 is easily explained by the fact that benzene has considerable affinity for trichloracetic acid and also for rubber. In imbibing the benzene therefore large amounts of trichloracetic acid are also absorbed with that hydrocarbon by the rubber. When we dissolve trichloracetic acid in benzene we really unite the acid with the benzene. In this homogeneous liquid, the solution, we have then the acid tied to the benzene; and because of the great affinity of the latter for rubber, the benzene solution of trichloracetic acid, the combination of the acid and the benzene, also has considerable affinity for rubber; and so the acid is also drawn into the rubber because it is united with benzene. To be sure, benzene and acid are not taken up by the rubber in the same proportions in which they occur in the solution, benzene being taken up in relatively larger amounts. This means that the solution is, to a certain extent, decomposed, *i. e.*, altered in concentration, by the rubber. When the latter, soaked with benzene and the acid, is in contact with water, the great affinity between water and the acid again comes into play and by virtue of it acid passes into the water, leaving the benzene behind in the rubber almost completely. Similar considerations hold in No. 13 where a solution of trichloracetic acid, water and benzene is separated from water by a rubber septum, except that here the acid passes through in lesser quantity, and minor amounts of water are undoubtedly also absorbed by the rubber, since in the solution the water is tied on to the benzene and the acid.[1]

[1] Compare Kahlenberg, "Über das Problem der Lösungen," Chem. Zeitung, 29, No. 81 (1905).

14. The inner liquid consisted of pure water, the outer of 0.1 normal solution of $AgNO_3$ in pyridine and the membrane of rubber. The liquid rose rapidly in the osmometer, reaching a height of 25 cm in four hours. The experiment was then stopped and the contents of the cell examined. It was found that pyridine had passed into the water, but no appreciable quantity of nitrate of silver. The entire content of the osmotic cell was evaporated to dryness, the residue extracted with a little water and a drop of nitric acid, and the filtered solution tested with HCl for silver, but none was found.

15. The inner liquid was a 0.1 normal $AgNO_3$ solution in pyridine, the outer liquid pure water, and the membrane parchment. The main current was from the water, through the parchment to the $AgNO_3$ solution in pyridine, for the level of the liquid in the osmometer rose to a height of about 18 cm in twenty hours. Water then goes into the cell, forming the main current, but both $AgNO_3$ and pyridine were also found in the water outside, showing a considerable counter-current toward the outer liquid.

16. The inside liquid consisted of 0.1 normal $AgNO_3$ solution in water, the outside liquid of 0.1 normal $AgNO_3$ solution in pyridine, the membrane being rubber. The main current was from the outer liquid to the inner one, the level rising in the stem of the osmometer. During the night the liquid filled the tube (which was about 32 cm long) entirely and ran over.

17. The outside liquid consisted of toluene, the inside liquid of 0.1 normal solution of $AgNO_3$ in pyridine and the membrane of rubber. The liquid rose 22 cm in the osmometer in seventeen hours. The main current consists of the passage of toluene through the septum to the pyridine solution of the $AgNO_3$; however, pyridine was also found in the toluene outside as were mere traces of silver nitrate.

18. This experiment was identical with No. 17 except that a parchment septum was employed. It was continued for four days and no change was observed. It seemed as though a slight lowering of the level of the inner liquid might

have taken place, so the contents of the cell were evaporated to dryness, the residue taken up with water and a drop of nitric acid and tested with HCl for silver, after having been filtered. Only the faintest indication of the presence of silver was thus obtained.

19. The inside liquid was 0.1 normal solution of $AgNO_3$ in pyridine, the outside liquid pyridine and the septum rubber. The liquid rose slowly in the osmometer, indicating the direction of the main current to be from the pyridine through the rubber to the solution. An examination of the outer liquid showed the presence of only a very small amount of nitrate of silver. The experiment was repeated, using a much heavier piece of ordinary gray sheet India rubber as a septum, with the same result. And again it was repeated, using the rubber dam as a membrane once more, but supporting it by tying over the outside of it a piece of muslin. With this arrangement the liquid rose in the stem of the thistle tube to a height of 28.5 cm in eighteen days, remaining there constant for two days, and then receding slightly. The temperature was very nearly 17° throughout the test. The outer liquid was found to contain appreciable amounts of $AgNO_3$, but hardly an estimable quantity. This shows that vulcanized caoutchouc is practically impermeable for $AgNO_3$ under the conditions described; in other words that it is a "semipermeable" membrane.

20. The inner liquid was a 0.05 normal solution of $AgNO_3$ in pyridine, the outer pyridine, and the septum rubber. At 17° C no change whatever was observed after six days. After nineteen days a rise of about 0.5 cm of the liquid in the stem of the osmometer was observed. The outer liquid was then analyzed for silver nitrate. Only traces were found, not an estimable quantity. This shows that the membrane did not leak and that the so-called osmotic pressure of an $AgNO_3$ solution in pyridine which is 0.05 normal is practically nil at 17° C when vulcanized caoutchouc is used as the semipermeable membrane.

21. The inner liquid was a normal solution of $AgNO_3$ in pyridine, the outer liquid pyridine and the membrane rubber. The apparatus was kept at a temperature which varied gradually between —16° and —15° C. At the end of the second day the liquid in the osmometer had risen to a height of 7.2 cm, the temperature being —16°. At the end of the third day the height of the column was 15.6 cm, the temperature being —15°. The membrane was intact and but traces of silver were present in the outer liquid.

22. The inner liquid was a normal solution of $AgNO_3$ in pyridine, the outer liquid pyridine, and the membrane rubber. In this case a piece of common vulcanized rubber about 1 mm thick such as is used on foot-power laboratory bellows was employed. It was supported on each side by pieces of muslin and perforated steel discs, and the whole was then securely screwed to the lower end of an osmotic cell made of steel. The maximum pressure which was read on a closed manometer, using mercury between the air space and the inner liquid, was 14.95 atmospheres at 20° C. The membrane did not "leak," which was evident from the fact that only mere traces of $AgNO_3$ were found in the outer liquid, though the experiment was run for two weeks, the pressure remaining practically constant for five days. This steel osmotic cell consumed considerable time in its construction, and many difficulties had to be overcome in perfecting it and attaching the manometer to it. However, it is unnecessary to enter into a detailed description of the cell, since no special significance will be attached to the single result recorded here, it being given simply to show that a very considerable pressure may be produced by a normal solution of $AgNO_3$ in pyridine when it is separated from pure pyridine by vulcanized caoutchouc at 20°, whereas at —16° (No. 21) the pressure formed is practically insignificant.

Silver nitrate is insoluble in hydrocarbons, which shows that the affinity between that salt and hydrocarbons is slight. Now as caoutchouc is a hydrocarbon substance, the affinity

between it and silver nitrate would be slight. Pyridine has considerable affinity for silver nitrate. It dissolves the salt readily with evolution of a considerable amount of heat. Pyridine is soluble in all porportions in hydrocarbons—is consequently readily imbibed by rubber. When a silver nitrate solution in pyridine is placed in contact with rubber the latter soaks up pyridine, but also some silver nitrate with it, since the pyridine and the salt are bound to each other by mutual attraction. This accounts for the fact that traces of silver nitrate pass into the pyridine when it is separated from a silver nitrate solution in pyridine by means of a rubber septum as in experiments 19, 20, 21 and 22, though the main current is that of the passage of pyridine through the membrane to the solution. Thus the reason why caoutchouc is a "semi-permeable" membrane in these cases is given; and we should expect in all cases in which the solute employed is insoluble in hydrocarbons, like kerosene, benzene, etc., yet is soluble in pyridine, that vulcanized rubber will act as a "semipermeable" membrane when it is employed in separating pyridine from the pyridine solutions of such solutes. This has been confirmed in the case of cane sugar and lithium chloride which are soluble in pyridine yet insoluble in hydrocarbons. The experiments are given below. Conversely, when a substance is soluble in hydrocarbons as well as in pyridine, that substance will always pass through vulcanized caoutchouc in notable quantities when its solution in pyridine is separated from pure pyridine by means of the caoutchouc septum. Examples of such cases will also be found below. Though experiments 19 to 22 are only quasi-quantitative in character they are already quite sufficient to show that here the osmotic pressure does not follow the gas laws at all. The change of the pressure with temperature is very much greater than proportional to the absolute temperature; and again the pressure varies much more rapidly with change of concentration of the solute than is required by Boyle's law. Experiment 20 reveals the fact that at room temperature the

osmotic pressure of the 0.05 normal solution of $AgNO_3$ in pyridine is practically nil under the conditions described, while on the basis of the van't Hoff theory the osmotic pressure of this solution ought to be over an atmosphere. We have in No. 20 the case where the solution has been diluted to such a point that its affinity for additional pyridine is practically equal to the affinity between pyridine and the rubber, so that the latter can not be robbed of its pyridine content by the solution, and consequently the liquid in the osmotic cell does not increase in bulk.

The observations made in Nos. 14 and 16 are such as might have been foreseen, considering the fact that water has practically no affinity for rubber; that the latter has considerable affinity for pyridine; that water and pyridine are consolute liquids; and that silver nitrate, though soluble in water and pyridine, is yet not soluble in hydrocarbons and consequently has practically no affinity for rubber. Further, recalling that water is readily taken up by parchment and pyridine and toluene not, and considering these facts in connection with those already mentioned, the data obtained in Nos. 15, 17 and 18 are readily explained.

23. The inside liquid was a 7.06 percent cane sugar solution in pyridine, the outer liquid pyridine and the membrane rubber, supported by muslin tied over it. The liquid rose in the osmometer to a height of 22.7 cm in four days, the height after the second day being 21.8 cm. Sugar had not passed into the outer liquid except in mere traces.

24. This experiment was like No. 23 except that xylene was used as the outer liquid instead of pyridine. The liquid rose to a height of 16.4 cm in four days. Sugar was not present in the outer liquid in appreciable quantities, but pyridine was.

25. The inside liquid was a 1.2 percent solution of sugar in pyridine, the outer liquid pyridine and the membrane rubber supported by muslin. The temperature was kept at 22.°5 C. A rise of the liquid in the osmometer tube was noted

after five minutes. After three hours the column measured 4 cm; after twelve hours about 5 cm. Sugar did not pass through the septum in appreciable amounts. The experiment shows that the solution used is able to produce but a very feeble osmotic pressure.

26. The inner liquid was a 0.125 normal solution of sugar in pyridine, the outer liquid pyridine and the septum rubber supported by muslin. The whole was kept at 0° C. After three days the liquid had risen only 0.5 cm in the osmometer tube; after five days, the rise was but 1.9 cm. The membrane was intact, and practically no sugar had passed into the pyridine without.

27. This experiment was like No. 26 except that a 0.25 normal solution of sugar was used as the inner liquid. The temperature was kept at very nearly —16° C. During the first day the liquid rose to 9.5 cm in the osmometer; on the second day the column measured 13.5 cm; and on the fourth day 17.5 cm. The membrane was intact and only very slight amounts of sugar were present in the outer liquid. The same experiment performed at room temperatures showed a very rapid rise of liquid in the osmometer tube—see pressures measured in the quantitative measurements described below.

28. The inner liquid was a saturated solution of LiCl in pyridine, the outer liquid pyridine and the septum rubber. The liquid rose in the osmometer and LiCl did not pass through the septum into the outer liquid in appreciable quantity.

Experiments 23 to 27 show that vulcanized caoutchouc is a "semipermeable" membrane when it separates sugar solution in pyridine from pure pyridine. The data lead one further to the conclusion that the gas laws do not govern the phenomena, which the measurements to be detailed later confirm. No. 28 shows that when LiCl is used as solute in an otherwise similar experiment, the rubber again acts as a semipermeable septum. The reasons for this behavior have already been discussed in connection with the $AgNO_3$ solutions.

29. The inside liquid was 0.1 normal $AgNO_3$ in pyridine, the outside liquid a saturated solution of cane sugar in pyridine, the membrane being rubber. The level in the osmometer fell, showing the current to be from the $AgNO_3$ solution to that of the sugar. On further examination it was found that $AgNO_3$ had also passed into the sugar solution but in small amount.

30. This experiment was identical with No. 29 except that parchment was used as the septum. The test was continued for three days. No change was observed.

In the light of what has already been said, it is clear that the results in Nos. 29 and 30 are such as might have been anticipated.

31. The inner liquid was a solution of $FeCl_3$ in toluene, the outer toluene, the membrane rubber. The main direction of flow is toward the solution, but $FeCl_3$ also passes through the membrane in considerable quantity, which was to have been expected since this salt is soluble in hydrocarbons. The $FeCl_3$ gradually disintegrates the septum.

32. This experiment was identical with that of No. 31 except that iodine was used as the solute instead of $FeCl_3$. The iodine also passed through the rubber, as was to have been expected; and it disintegrated the septum more rapidly than did the $FeCl_3$. The liquid, however, first rose in the osmometer.

33. The inner liquid was a solution of copper oleate in benzene, the outer benzene and the septum rubber. The liquid in the osmometer rose to a height of 20 cm, showing the main current to be toward the solution; however, large amounts of copper oleate passed through the rubber into the outer benzene. This was to have been expected, since copper oleate is soluble in hydrocarbons.

34. This experiment was identical with No. 33 except that parchment was employed as the septum in place of rubber. No change whatever took place, which was to have been anticipated since none of the ingredients touching the membrane have sufficient affinity for it.

35. This experiment was like No. 33, except that the copper oleate was dissolved in pyridine, and pyridine was used as the outer liquid. Again the main current was toward the solution, but copper oleate passed into the outer pyridine in considerable quantity, which is quite in harmony with the theory advanced.

When we think of a large molecule like that of copper oleate readily traveling through vulcanized caoutchouc as in No. 35, and that under like conditions cane sugar, $AgNO_3$, and LiCl do not pass through that septum, it certainly must convince us that the membrane does not act as a sieve. Again No. 34 shows that parchment is not a "porous" material as is so commonly assumed from osmotic experiments with aqueous solutions in which it is employed as septum.

36. The inner liquid was a strong solution of sodium oleate in water, the outer liquid water and the septum rubber. No change occurred.

37. The experiment was like 36 except that parchment was employed as the septum. In this case sodium oleate was found in the outer water, though the inner liquid showed slight increase in bulk.

Sodium oleate, though soluble, in water is insoluble in hydrocarbons; bearing this fact in mind, the results in Nos. 36 and 37 are readily explained.

38. The inner liquid consisted of a normal solution of naphthalene in pyridine, the outer liquid was pyridine and the membrane rubber. Practically no change in level occurred, but large quantities of naphthalene passed into the pyridine without.

39. The inner liquid was a normal solution of camphor in pyridine, the outer pyridine and the septum rubber. Practically no change in level occurred, but considerable amounts of camphor appeared in the outer liquid.

40. The inner liquid was a saturated solution of camphor in 99.5 percent alcohol, the outer liquid 99.5 percent alcohol and the septum rubber. After half an hour a slight lowering

of the level of the liquid in the osmometer was noted; it continued to go down for three days, when the experiment was stopped. Much camphor had passed into the alcohol without.

41. The inner liquid was a saturated solution of camphor in toluene, the outer liquid toluene and the membrane rubber. The liquid at once rose rapidly in the osmometer. In nine hours it reached a height of 32 cm. It continued to rise for three days, the duration of the experiment. Large quantities of camphor had passed through the septum into the outer toluene. Camphor is very soluble in toluene.

That naphthalene and camphor should pass through rubber was to have been expected, Nos. 38 to 41, since these substances are very soluble in hydrocarbons. In No. 40 the main current is from the solution of camphor in alcohol to the alcohol, while in 41 the main current is from the toluene to the camphor solution in toluene. This occasions no surprise when it is borne in mind that toluene is imbibed much more rapidly and more copiously by rubber than is alcohol, and that an alcoholic solution of camphor is imbibed by rubber more rapidly than is alcohol. Again, remembering that it is the relative rate of inflow and outflow which determines whether the bulk of the liquid in the osmotic cell will change or not under given conditions, the results in 38 and 39 are readily explained.

42. In the osmometer was placed a solid block of camphor in form of a cube which weighed 2 grams; the outer liquid was 99.5 percent alcohol, and the membrane rubber. The osmometer was immersed in the liquid so that the membrane was slightly below (about 0.5 cm) the surface of the liquid. The arrangement is shown in Fig. 5. After five minutes there seemed the least evidence that the camphor was being attacked, but even after four hours, there was but little further change. Since alcohol is not very readily imbibed by rubber this occasioned no surprise.

43. This experiment was identical with No. 42, except

that toluene was used instead of alcohol. Plain evidence that the camphor was dissolving appeared in three minutes. In forty minutes the solid camphor had all disappeared and was found in very large quantities in the outer liquid. The

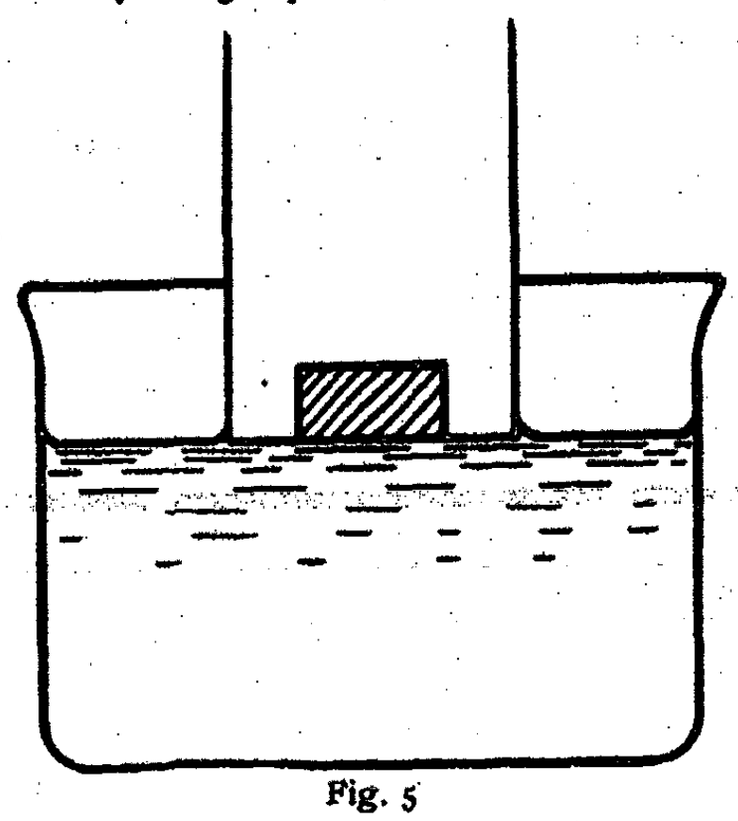


Fig. 5

membrane became much distended, bulging downward. The level of the liquid was alike in and outside after four hours, it having risen slightly on the inside.

44. This experiment was like No. 42 except that xylene was employed instead of alcohol. The observations were practically identical with those of No. 43 where toluene was employed, which might have been expected.

45. This experiment was also like No. 42 except that pyridine was employed instead of alcohol. After four minutes it was evident that the camphor was being attacked. A very thin layer of liquid, less than 1 mm thick, appeared on the upper side of the rubber. In four hours all the camphor had gone through the rubber into the pyridine, leaving a depth of solution of only about 1 mm on the upper side of the membrane. During the process the membrane became somewhat distended and bulged upward toward the camphor.

46. In this case the arrangement was again like in No. 42, except that CCl_4 was employed instead of alcohol. After

about four minutes it was evident that the block of camphor was beginning to disappear. In forty-three minutes the whole block was gone, having passed through the rubber into the CCl_4, leaving on the upper side of the membrane a camphor solution less than a millimeter deep. The membrane became distended and bulged upward. After four hours, the liquid on the upper side of the membrane was from 1 to 2 mm deep.

47. This experiment was also like No. 42 except that CS_2 was used as the liquid instead of alcohol. After four minutes it was clearly evident that the block of camphor was being attacked. After thirteen minutes a thin layer of liquid was visible on the upper side of the rubber. After forty-five minutes all solid camphor had disappeared, having passed through the rubber into the CS_2, leaving on the upper side of the membrane a solution about 3 to 4 mm deep. After four hours the membrane appeared very much distended, bulging downward, the liquids in and outside being on a level.

48. In this case a cube of paraffine of rather high melting-point (70°) was separated from 99.5 percent alcohol by means of a rubber septum, the arrangement being as described in No. 42. After twenty-four hours the lower corners and edges of the paraffine cube appeared slightly rounded. No liquid was visible on the upper side of the rubber, however. After three days the large bulk of the paraffine was still intact, though it was distinctly evident that the substance was slowly passing through the rubber septum into the alcohol beneath, without any liquid layer appearing on the upper side of the membrane.

49. This experiment was identical with the preceding one, No. 48, except that toluene was used instead of alcohol. In this case solution gradually accumulated on the upper side of the rubber, though paraffine passed through into the toluene on the outside. After twenty-four hours only about one-eighth of the paraffine was left undissolved and the liquid on the inside was practically on a level with that on the outside. Much paraffine was found in the outer liquid.

50. In this case the cube of paraffine was separated from pyridine by means of rubber, the arrangement being as described in connection with No. 42. The observations were practically the same as when alcohol was employed, No. 48.

51. The experiment was identical with the preceding one No. 50, except that CCl_4 was used instead of pyridine. After twenty-four hours about three-fourths of the paraffine was still left in the solid state; it floated on the layer of liquid which had formed on the upper side of the rubber. Considerable paraffine had gone through the septum into the CCl_4 below. The membrane was much enlarged and bulged downward. After two days, all the paraffine had dissolved and the liquids in and outside were nearly on a level.

52. About 2 grams of dry powdered $AgNO_3$ was placed on the upper side of a rubber membrane, the lower side being bathed by pyridine. The arrangement was as pictured in Fig. 5, the powdered $AgNO_3$, which was spread out over the surface of the membrane, taking the place of the block represented in the figure. The experiment then was the same as No. 45 except that the $AgNO_3$ was used in place of camphor. After seven hours no liquid was visible on the upper side of the membrane. Pyridine had, however, passed into the silver nitrate and formed a solid addition product with it. No appreciable amount of $AgNO_3$ had passed into the pyridine without. After twenty-four hours all the $AgNO_3$ had dissolved and the liquid in the osmometer had risen to a height of about 1.5 cm and continued to rise. After four days the experiment was stopped and the outer liquid examined for $AgNO_3$. It was, however, found to be present only in mere traces. This shows that vulcanized caoutchouc is indeed a good "semipermeable" membrane in this case.

Considering experiments Nos. 42 to 52 in which solids were separated from liquids by means of rubber septa, it is evident that whether the solid will pass through the membrane or not depends on the nature of the solid, the membrane and the liquid employed. Furthermore, if the sub-

stance composing the solid does make its way through the septum, the fact as to whether the action is accompanied with an accumulation of liquid on that side of the septum occupied by the solid or not is clearly determined by the rate with which the solution formed is absorbed by the membrane (which is determined by the mutual attraction or affinity of the saturated solution and the membrane for each other) and also by the rate with which the pure solvent is imbibed from the other side.

Now it is well known that camphor dissolves very readily in hydrocarbons and consequently has considerable affinity for rubber, and we should therefore expect it to pass through the latter when it is employed as an osmotic membrane. An alcoholic solution of camphor is more readily imbibed by rubber than is pure alcohol, and so it occasions no surprise when in No. 42 we find the block of camphor slowly making its way through the rubber septum into the alcohol, and without the appearance of liquid on the side occupied by the camphor. The action is slow because alcohol is not imbibed rapidly or copiously and because the septum holds on to the strong camphor solution very tenaciously, so that only a small portion of the camphor thus saturating the rubber is washed out of the latter by the alcohol on the other side.

When the same experiment is performed using a hydrocarbon as the liquid instead of alcohol, Nos. 43 and 44, the action goes on very much more rapidly on account of the great affinity between rubber and the hydrocarbon or a camphor solution in a hydrocarbon. The strong camphor solution is so greedily absorbed by the rubber that but little liquid appears on the upper side of the membrane while the solid camphor lasts, and it is as though the solid camphor were passing through the rubber septum by mere contact with it. The process reminds one strikingly of the manner in which solid food placed in the alimentary canal is digested and absorbed. Here the presence of the food in contact with the walls of the tract excites the flow of the digestive juices toward

the solids; the latter are acted upon and the resulting liquid is absorbed by the walls of the canal. In our experiments the camphor in contact with the rubber saturated with a hydrocarbon excites a flow of hydrocarbon toward it. The hydrocarbon acts on the camphor "dissolving" it, and the resulting solution is then so rapidly absorbed by the septum as to leave no liquid on the side occupied by the camphor.

When as in No. 45 pyridine is used instead of a hydrocarbon, the camphor is still absorbed, but not as rapidly, for pyridine is not taken up by rubber as readily or as copiously as are hydrocarbons; neither has camphor so great an affinity for pyridine as for hydrocarbons. On the other hand, camphor very rapidly disappears when CCl_4 or CS_2 (Nos. 46 and 47) are employed, for these substances have great affinity for rubber and also for camphor.

When paraffine instead of camphor is separated from alcohol, toluene, pyridine or carbon tetrachloride by means of rubber, Nos. 48 to 51, the action is in all cases slower, which fact is readily comprehended when it is borne in mind that camphor dissolves more readily in the liquids named than does paraffine.

Finally in No. 52, where solid silver nitrate is separated from pyridine by rubber, we have an illustration of a typical case in which the liquid accumulates very greatly on the upper side of the membrane. Here the solute has very little affinity for the rubber, and so the solution of the salt practically does not get into the septum on account of the fact that pure pyridine is more readily imbibed and silver nitrate is difficultly soluble in rubber soaked with pyridine, that is to say, in a hydrocarbon diluted with pyridine. If a block of cane sugar or one of chloride of lithium were separated from pyridine by means of a rubber septum, the action would be similar to that observed in the case of silver nitrate, No. 52. The same would be true if any solid which is soluble in pyridine yet not soluble in hydrocarbons were separated from pure pyridine by means of a rubber membrane. It would be

interesting to test this in the case of more substances which are insoluble in hydrocarbons and yet are soluble in pyridine, but the number of such substances is rather limited, for it must be remembered that pyridine is itself nearly a hydrocarbon in character and is consolute with hydrocarbons.

Qualitative Tests with Animal and Vegetable Membranes

A number of qualitative tests were made with membranes of organic origin. It was thought best to place the results of these experiments on record here, though it is contemplated to take up the whole matter of the action of organic membranes separately at some later date.

Various animal membranes were tested as to their permeability for sodium chloride, urea and cane sugar. The membranes were stretched over square wooden frames quite loosely so as to form bags or pockets into which one liquid was placed; these bags were then suspended in the outer liquids in such a manner that only the lower sagging part, and not the upper edges were in contact with the outer liquids. As membranes to be tested were selected the pericardium, diaphragm, small intestine, large intestine, stomach, aorta, urinary bladder and gall cyst of a young ox. The animal was perfectly sound and normal and about three years old. The membranes were used soon after the animal had been killed. On the upper side of each membrane was placed an aqueous solution containing 23.4 grams of sodium chloride, 40 grams of urea and 342 grams of cane sugar in 2000 cc, while the lower side of the membrane was immersed in pure water, the arrangement being as already described. It was found that in case of all of the membranes mentioned the sodium chloride passed through more rapidly than the urea and sugar, which fact was established by examining the outer liquid from time to time during the first four hours. After twenty-four hours, besides much salt very considerable quantities of urea and cane sugar had gone through all the membranes. A special test made by separating water from

an aqueous solution of sodium sulphate by means of the stomach membrane, showed that the latter is permeated but slightly by sodium sulphate, for the amounts of the latter salt in the outer liquid were but small.

The vegetable septa employed consisted of the rinds of California oranges and grape fruit and Florida grape fruit. The grape fruit, also called shaddock, is the fruit of *Citrus decumana*. In each case the fruit was carefully cut in two transversely with a sharp knife, so that the halves after careful removal of the pulp formed two cups. Each half rind was filled to about half of its capacity with the liquid to be tested and then suspended in pure water so that the latter was about on a level with the liquid in the rind. The suspension of the rind was accomplished by means of fine aluminum wire run through small holes pricked through the upper edges of the rind. Each experiment was continued for twenty-four hours, unless otherwise stated. It was found to be impracticable to continue the experiments much longer, for the rinds after being immersed in water for a considerable time undergo alteration, becoming soft and losing their waxy outer coating.

With the arrangement as just described and employing water as the outer liquid and an aqueous solution as the inner liquid, it was found that sodium chloride readily passes through orange skins, but sodium sulphate very much less readily. Indeed, only traces of the latter salt were found in the outer liquid even when strong solutions were employed. Again, urea readily goes through the orange rinds, but sugar passes through only in very small amounts. When an aqueous solution of potassium alum was used it was found that a slight amount of potassium sulphate appeared in the outer water, but no aluminum sulphate, showing that the latter ingredient is left behind during the time of the experiment at least.

In the upper half of the rind of a Florida grape fruit was placed 100 cc of a solution containing 10 grams sodium chloride plus 10 grams of sodium sulphate. The rind so charged was

suspended in distilled water as above described. The outer water had a volume of 500 cc. Tests of the outer liquid showed that the NaCl was passing through much faster than the Na_2SO_4. This experiment was run for seven days; the rind did not seem to be altered much.

The lower half of the rind of a California grape fruit containing 70 cc of an aqueous solution which contained 10 grams of NaCl plus 10 grams of sugar in 100 cc, was suspended in a dish in 300 cc of water. It was found that the sugar passed through the rind much more slowly than the salt. The experiment was continued for seven days.

A similar experiment in which 80 cc of an aqueous solution containing 10 grams sugar plus 10 grams urea in 100 cc was placed in the upper half of the rind of a California grape fruit suspended in a dish containing 400 cc water, yielded the result that both urea and sugar pass through the rind, but the latter more slowly. After twenty-four hours sugar may be detected in the outer liquid with Fehling's solution. The urea acts on the rind, thickening and hardening it. Much urea is thus retained in the rind, also considerable amounts of sugar. These facts were determined by an examination made after the experiment had run for seven days.

To 70 cc of a saturated solution of boric acid in water 10 grams of sugar were added. This solution was placed in the upper half of the rind of a California grape fruit, the outside being bathed by water. The experiment was continued for five days, the rind remaining intact and practically unaltered during this time. Only traces of boric acid passed through the rind. Sugar passed through slowly, but at the end of five days it was found in the outer liquid in considerable quantity.

It was found, further, that in dilute aqueous solutions H_2SO_4, HCl and HNO_3 readily pass through the skins of grape fruit, but the rinds are much altered by the acids, appearing shrunken and darkened in color. Citric acid passes through less rapidly than the mineral acids mentioned. It is apparently retained to a considerable extent in the rind.

The experiments made with the rinds of grape fruit were also repeated with the skins of California oranges, with practically the same results.

Quantitative Measurements of Osmotic Pressures

The quantitative measurements of osmotic pressures were made with so-called semipermeable membranes, that is to say, with membranes through which the solvent passes so much more readily than the solute, that the amount of the latter which goes through the septum is practically a negligible quantity. From what has been said above, it appears that the latter quantity is never absolutely nil, and that consequently there is really no such a thing as a semipermeable membrane, strictly speaking.

Now as has been intimated, the qualitative experiments above detailed enable one to foretell when a membrane will permit the solvent to go through so much more readily than the solute that the amount of the latter which traverses the membrane is so slight that the septum may be called semipermeable. From the ether, water, chloroform experiment, already described as a typical case of osmosis, it appears that the ether makes its way through the water into the chloroform because (1) ether is soluble in water and (2) chloroform has much more affinity for ether than has water, so that ether is extracted from the water layer by the chloroform; on the other hand, the water does not permit chloroform to pass into it and into the ether beyond to an appreciable extent, because chloroform is so very slightly soluble in water even when the latter is impregnated with ether.

Holding these things in mind let us look for the proper solvent and solute to employ with rubber as the membrane so that the latter shall be semipermeable. It must first be remembered that rubber (vulcanized caoutchouc) is practically a hydrocarbon. The rubber employed was of excellent quality and was almost the pure gum. On analysis it was found to contain 0.38 percent ash, and a Carius determination

yielded 0.30 percent chlorine and 0.95 percent sulphur. Before the analysis was made the sample was wiped superficially, washed with distilled water, dried with filter-paper and finally left in a desiccator over strong sulphuric acid for twenty-four hours. It is evident that in order to pass through a rubber membrane a substance must be taken up by the rubber, the rubber must imbibe the substance; in other words, the substance must be soluble in rubber.[1] Again the liquid bathing the other side of the rubber must be capable of extracting the imbibed substance from the rubber, thus completing the transference. On the other hand, those substances which are not soluble in rubber, *i. e.*, are not taken up by the rubber, will obviously not pass through the latter. And so what is required is a solvent which will readily be taken up by rubber, without, however, disintegrating the same, and a solution of such a character that the solute shall not be soluble in rubber. The less affinity the solute has for rubber the better, for then when the solution is brought into contact with the rubber the latter will imbibe practically only solvent to the exclusion of solute, thus leaving the solution slightly more concentrated, that is to say, making a partial separation of solvent and solute.

In casting about for a suitable solvent very many substances were tried. It was, of course, desirable to secure a solvent that was not too volatile at ordinary temperatures or too obnoxious. In the course of this work it soon became evident that water, alcohols and, in general, compounds containing considerable hydroxyl, relatively speaking, are not suitable for they are not taken up readily enough by rubber nor in sufficient quantity. On the other hand many compounds, like hydrocarbons, their halogen substitution products, carbon disulphide, ether, etc., though taken up readily by rubber and in considerable quantity, gradually act upon the latter to such an extent as to form with it a very soft,

[1] The act of such solution or imbibition is really mutual; *i. e.*, the rubber attracts the substance in question, and the latter in turn attracts the rubber.

sticky mass, or even a liquid, a combination or solution then of such mechanical properties as to be entirely unsuitable for quantitative osmotic experiments. After trying a large number of liquids, pyridine was finally taken as being the most suitable for the purpose in hand. From its very nature pyridine is a substance which would perhaps be expected to fulfil the requirements. Its high carbon and hydrogen content make pyridine almost a hydrocarbon; indeed, it dissolves in hydrocarbons in all proportions. Since rubber is a hydrocarbon, we should expect it to imbibe pyridine readily. It was found that pyridine is imbibed by rubber, increasing the bulk of the latter somewhat to be sure, but without otherwise materially altering the mechanical properties of the rubber. Indeed, I found that vulcanized caoutchouc may even be boiled in pyridine for hours, in which case there is a slight amount of material extracted from the rubber, giving the liquid a brownish color; but the rubber is not disintegrated or affected materially otherwise. The rubber used as membranes in the actual quantitative measurements was in fact thus extracted with boiling hot pyridine. After such treatment, rubber, when dried, has practically all of its original properties; it is perhaps a little easier to rupture it by stretching it hard. It might at first be somewhat surprising that pyridine does not disintegrate rubber more. However, while pyridine is closely akin to hydrocarbons and consolute with them, it must be borne in mind that water, which has but little affinity for hydrocarbons, also is consolute with pyridine. Pyridine is then a rather unique substance, and it is hardly surprising that it should be imbibed by rubber sufficiently for the purpose in hand without unduly disintegrating it. Direct experiment showed that at room temperature (about 20° C) 100 grams of the vulcanized caoutchouc used imbibed 144.42 grams of pyridine in twenty-four hours, while the amount imbibed in seventeen days was 145.17 grams.

A suitable solute would be one that is soluble in pyridine yet insoluble in hydrocarbons. For instance, a substance soluble in petroleum or benzene would in general also be

soluble in pyridine, but it would also be soluble in rubber (a hydrocarbon) and hence would pass through the latter. Thus oleic acid, the oleates of the heavy metals, ferric chloride, naphthalene, camphor are soluble in hydrocarbons, are consequently readily taken up by rubber, and when dissolved in pyridine pass through the rubber when the latter in an osmotic experiment separates the solution from pure pyridine. Because of the peculiar nature of pyridine already alluded to above, this liquid dissolves a goodly number of substances which are insoluble in hydrocarbons. The solubility of such substances in pyridine is, to be sure, rather limited as to quantity as a rule. So cane sugar, silver nitrate, lithium chloride are insoluble in hydrocarbons and yet reasonably soluble in pyridine. One would consequently expect that when solutions of either of these substances in pyridine be separated from pure pyridine by means of a rubber septum, practically none of the solute would pass through the rubber; in other words, the latter would be practically impermeable for sugar, silver nitrate and lithium chloride. Now this is actually what was found in the qualitative tests described above. These substances pass through rubber in extremely slight quantities which are quite comparable with the amounts of cane sugar that pass through the much studied copper ferrocyanide membrane, when it separates water from an aqueous sugar solution. However, on account of the fact that sugar has a high carbon and hydrogen content, one would expect it to have more affinity for a hydrocarbon than either silver nitrate or lithium chloride, and that consequently it would pass through rubber a little more readily than these salts. Experiment has also shown that this is actually the case, though, as stated above, the amount of sugar which passes through the rubber membrane is quite small.

The quantitative measurements of osmotic pressures were then made by using solutions of cane sugar, lithium chloride, and silver nitrate in pyridine, these solutions being separated in each case from pure pyridine by means of a mem-

brane of vulcanized caoutchouc previously treated with boiling hot pyridine so as to extract any soluble ingredients. It was not the purpose of the quantitative measurements of osmotic pressures to produce and measure enormous pressures, though as was shown above in No. 22 a pressure of approximately fifteen atmospheres was actually measured in the case of a normal solution of silver nitrate in pyridine. The efforts were rather directed toward determining with a sufficient degree of accuracy moderate pressures, using different concentrations of the solutions employed at several different temperatures.

The osmotic cells were made entirely of glass, excepting, of course, the surface actually closed by the membrane itself,

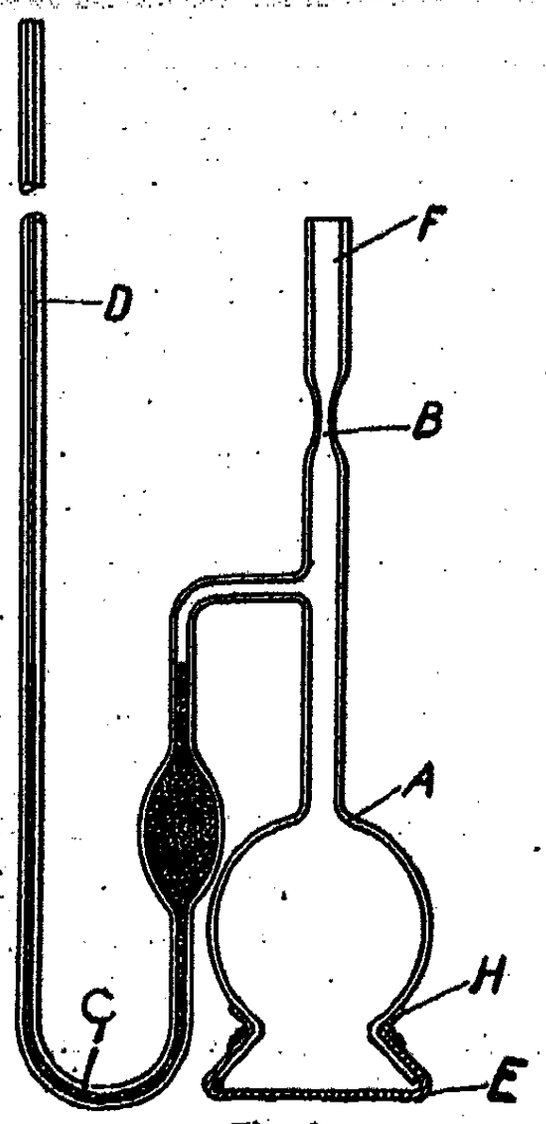


Fig. 6

The different parts of the cells were fused together so as to form one piece, thus avoiding cemented joints of any kind. Fig. 6 shows how these cells were made. To a stout, care-

fully-made thistle tube having a flare of about 45° at E a T was attached, the tube being provided with a bulb and bent as shown in the figure, C. To C was fused a manometer tube D having a bore of about 0.5 mm; this tube was made as long as the experiment required. The small bulb and bent part of the tube C contained mercury. At B the tube was somewhat contracted as shown, and after putting the required amount of pure, clean mercury into the apparatus and filling the rest of it with the solution to be tested through the orifice F by means of a capillary funnel tube, the apparatus was carefully heated at B by means of a small flame and finally drawn off, leaving the whole securely sealed. With practice this part of the operation may be so performed that practically no air bubble remains in the apparatus after the tube has been drawn off at B.

Before placing the mercury and the solution into the cell, however, the membrane must be securely put into place. It is first of all essential that the opening of the bell of the thistle tube E be as nearly circular as possible, and that the points on the outer edge of the orifice lie in very nearly the same plane. The rubber membrane consisted of a high quality of sheet rubber as is used by dentists. Its ash, sulphur and chlorine content have already been given above, and it has also been stated that the material was extracted with hot pyridine before using it. The rubber so prepared was carefully tied over the orifice at E. In this process it was stretched only moderately so as not to thin it unduly.[1] In tying the membrane on, the rubber was always stretched to such an extent, however, that no folds whatever remained where it touched the glass. With proper care it is possible to get a smooth surface of rubber to rest snugly against the surface of the glass. The rubber was finally securely fastened into place by carefully winding the whole surface from H to E smoothly and closely with moderately fine thread. When

[1] When finally in place, the thickness of the membrane was only a small fraction of a millimeter.

these precautions are observed one hardly ever fails to get a perfectly tight joint between the glass and the rubber, which is so all-essential.

The next step consisted of supporting the membrane so that it would withstand pressure. To accomplish this there was first tied over the membrane a piece of smooth, soft yet strong muslin. This cloth was drawn tightly over the membrane, and securely tied on by winding moderately fine yet strong thread over it smoothly and evenly from H to E. It is of course impossible to get rid of folds in the cloth where it is tied on the surface H to E, but it is quite possible to distribute these folds fairly evenly around the circumference, in such a manner that the cloth where it actually touches the rubber on the mouth of the thistle tube and just at the edge at E, lies perfectly smoothly and snugly against the surface of the membrane giving it proper support. After this a circular perforated disc of stout sheet steel made of proper size so as just to cover the lower end of the thistle tube was placed on the muslin covering the rubber; and this disc was then securely held in place by tying over it very firmly another piece of strong muslin by means of stout thread evenly and tightly wound on as in the previous cases. Thus there was the rubber tied on the glass, then the muslin snugly covering and supporting the rubber, then the steel disc sieve pressing against and supporting the muslin, and finally the outer layer of muslin firmly holding the disc in the proper position. The perforations in the disc were about 1 mm in diameter and the disc itself was about 0.5 mm thick. By observing closely the precautions here laid down, cells were practically always obtained without fail which were perfectly tight, rigid and capable of withstanding pressures up to the point of bursting the glass bell of the thistle tube. Furthermore, on taking such an apparatus apart even after experiments that had continued for weeks, the membrane was found to be intact and in perfect condition. Experiments demonstrating that such membranes do not leak have already been given above,

Nos. 1 and 2. We have here then a simple, direct and certain method of preparing so-called semipermeable membranes for osmotic pressure measurements, which are yet not precipitated membranes; and furthermore we know *why* the membranes are semipermeable for the solutions that come into question.

After the membrane has been put into place as described, the apparatus is charged with the required amount of mercury and then with the solution to be tested, the tube being drawn off at B before the small flame of a blowpipe so as to leave no air in the apparatus. The latter is then placed in a large vessel containing the pure solvent, and the rise of the liquid in the manometer tube is observed from time to time, a pair of sensitive thermometers graduated to 0.1° being placed in the solvent near the osmometer to indicate the temperature. The apparatus was set up in a basement room, whose temperature changed but slightly and only very gradually during the course of the experiments. It is highly essential that the temperature be kept as constant as possible during the experiments and that sudden fluctuations be avoided. From what has been said it is evident that the experiments were finally set up in much the same way in which Pfeffer performed his tests, only in this case additional care was taken to cover up the dish so as to minimize evaporation and to protect the surface of the pyridine from the moisture of the air. All measurements were made with the open manometer and the height of the mercury column was estimated to within 1 mm in each case. It was found to be quite needless to measure more closely than this, for the results of separate duplicate experiments showed greater variations as a rule.

I will first give the results of the experiments performed by using the method just described, which method, though it is the usual one, had to be modified later in one important particular in order to secure reliable results. The individual experiments are numbered consecutively with those preceding so as to facilitate future reference to them.

53. The liquid in the osmometer was a solution of cane sugar in pyridine containing one-fourth of a gram-molecule per liter of the solution. The outer liquid was pure pyridine. The experiment was run in triplicate, that is, three separate individual tests were made with the same solution. The temperature in each case was 17°.5 C. (*a*) In the first of these experiments the pressure came up slowly, remaining nearly constant after the second day. The experiment was nevertheless allowed to go on for nine days when the pressure was finally measured and found to be 186.2 cm at 17°.5 C. Before discontinuing the experiment, the whole of the outer vessel was packed in melting ice for ten hours. The mercury column became constant at 125 cm after three hours and remained there for the remaining seven hours. The temperature was then permitted to rise slowly and after three days the mercury column was 159.5 cm high, the temperature being 16°.4. When the whole had finally reached the temperature 17.5, the mercury column was again 186.0 cm high. This then would seem to be pretty good evidence that the maximum pressure had indeed been reached. During the operation care was taken not to disturb the apparatus by jarring it in any way. The outer liquid was found to contain traces of sugar, but the exact amount was not determined. (*b*) In the second independent yet perfectly similar experiment, the pressure also rose gradually, changing but slightly after the second day. The temperature was kept at 17°.5 C, and at the end of eleven days the column of mercury measured 155.6 cm. This experiment was then allowed to run for four days longer. At eight in the morning of the fourteenth day the mercury column measured 166.4 cm at 16°.4 C, while at five in the afternoon of the fifteenth day it measured 166.7 cm at 16°.0 C. As in the previous case, care was taken not to jar the apparatus during the experiment. In this case, too, traces of sugar were found in the outer liquid. (*c*) In a third similar experiment the pressure also increased but little after the second day. The experiment was stopped at the end of

four days in this case, when the mercury column was 107.4 cm high, the temperature being 17°.5 C. Only traces of sugar were found by testing the outer liquid.

It will be noted that the highest pressure was observed in (*a*). In this experiment the pressure came up more rapidly than in the other two cases, accomplishing 115 cm in the first twenty-four hours. The discussion of the causes of the discrepancies in the results of (*a*), (*b*) and (*c*) will be left until a little later.

54. This experiment was performed in duplicate. The arrangement was exactly like that in No. 53 except that the liquid in the osmometer consisted of a solution of cane sugar in pyridine containing one-eighth of a gram-molecule per liter of the solution. (*a*) The pressure rose slowly, increasing but slightly after forty-eight hours. On the sixth day the mercury column measured 62.4 cm, the temperature being 17°.5 C. The whole was then surrounded with melting ice, and after two hours the mercury column measured 0.2 cm; at the end of ten hours the pressure was 0.6 cm. The temperature then gradually rose during the night as the ice disappeared. At 14°.5 C the column measured 48.8 cm and at 17°.5 C it again came up to 62.0 cm, nearly where it was before the chilling process. In this case the experiment was left set up for five days longer, when the column measured but 43.6 cm at 18° C. Sugar was found to be present in the outer liquid in small amount. (*b*) This was a duplicate of (*a*). The observations made were practically the same as in (*a*) except that the pressures were different. The chilling process with ice was omitted in this case. After two days the pressure increased but slightly. On the third day it was measured carefully and found to be 52.8 cm at 17°.5 C. During the next two days the temperature fell very gradually to 14°.5 C and the column then measured 42.5 cm. The temperature then rose gradually to 18° C during the succeeding three days, when the pressure was 46.3 cm.

55. In this experiment the inner liquid was a solution

of cane sugar in pyridine containing 0.25 gram-molecule per liter of solution, while the outer liquid was a solution of cane sugar in pyridine containing 0.125 gram-molecule per liter of solution. The pressure rose slowly, the mercury column reaching a height of 137.5 cm at 16°.8 C. By far the most of this was accomplished during the first two days. The final measurement just given was taken after thirty days. The experiment was then left undisturbed for twenty-six days longer. The pressure began to diminish gradually and finally measured only 89 cm, when the experiment was discontinued. The membrane when examined at the end of this time was to all appearances intact and but slightly changed, if at all.

56. Two experiments were made with solutions of cane sugar containing 0.25 gram-molecule of cane sugar per liter of solution in pyridine as the inner liquid, and pure pyridine as the outer liquid, employing in this case, however, a common thick sheet rubber—such as is used on the ordinary foot-power laboratory bellows—in place of the finer vulcanized caoutchouc used in the other experiments. The experiments were conducted side by side as duplicates of each other. The pressure rose gradually, the mercury column reaching a height of 43.0 cm in one case and 39.5 cm in the other at 22° C. The rubber was found to be much softened when examined at the end of ten days, the duration of the experiments. The maximum pressure was practically reached after forty-eight hours. The pressure diminished gradually after seven days. Small amounts of sugar were found in the outer liquid, though the exact amount was not determined.

From the results just detailed it is evident that the methods employed are not capable of yielding concordant values. Though only attempts to measure osmotic pressures of sugar solutions in pyridine have been described, similar experiments were made using lithium chloride and silver nitrate solutions in pyridine. In these cases the results were no more concordant than in those in which sugar was solute.

At first it was thought that the difficulty lay in the membrane itself, the initial experiments having been performed by using the sheet rubber without further treatment; but actual tests showed that whether the rubber was previously extracted with boiling hot pyridine or not made no perceptible difference in the results. It will be noted that one set of experiments was made, using a common thick sheet rubber (No. 56). In this set the results were very different from those obtained with the thin rubber of high grade (No. 53), and yet the duplicates did not differ from each other more than when thin rubber was used. It was also determined by several trials that the non-concordance of the results of duplicate experiments could not be laid to the fact that in some cases the rubber was stretched rather more than in others. It was not to be expected, of course, that the maximum pressure would be reached in the same time in two experiments that were similar, for the areas of the surfaces of the membranes and their thickness were not exactly the same. It might further be possible that the differences in pressure observed in the experiments that were duplicates of each other occurred because slightly different amounts of sugar passed through the different membranes; in other words, that there was more leakage of solute in one case than in the other. Such leakage or lack of semipermeability would operate to diminish the osmotic pressure in two ways, (1) by directly letting material out of the cell as the pressure rises, and (2) by increasing the amount of solute in the outer liquid and so weakening the cause which creates the pressure. It is quite true that in all cases small quantities of sugar passed through the membranes, and that these were perhaps not always exactly the same. The qualitative tests made, however, always showed that the quantity which had passed through was very small and far below the amount required to produce a noticeable osmotic pressure with the apparatus employed during the time of the experiments. It will be recalled that a 1.2 percent solution of sugar in pyridine yields practically

no osmotic pressure (No. 25) and that the same is true of a 0.05 normal solution of silver nitrate in pyridine at room temperature (No. 20). Furthermore, when two similarly charged osmometers were set in one and the same outer vessel filled with pyridine, they nevertheless in general failed to indicate identical pressures. All this led me to the conclusion that the non-concordance of the pressures measured could not be due to leaks, defects or various degrees of "semi-permeability" of the membranes.[1]

I confess that I was about at my wits' end to understand why such duplicate experiments made as nearly as possible the same in every way should yet yield results that were not more concordant. In all, some seventy independent trials had been made, in which great care had been used to get the experiments alike, but to no avail. Yet the membranes were not defective. One day after measuring carefully the height of the mercury column in one of the experiments which had been running for two weeks and in which the pressure had changed inappreciably for several days, I happened to brush against the apparatus in such a way as to

[1] Measurements of the electrical resistance of the membranes were also made which further established this fact. Placing on each side of the membrane of an osmotic cell, such as was employed in the pressure measurements, a circular platinum electrode about 2.5 cm. in diameter, so that the planes of the electrodes were parallel to that of the membrane, and that the metallic surfaces were close to the membrane without actually touching it, the cell was filled with an aqueous saturated solution of NaCl and the same solution was used as the outer liquid. The electrodes were thus immersed in the saturated NaCl solution and the membrane separated them from each other. The electrical resistance between the plates was measured by means of the Kohlrausch method; but it was found to be so great that it was not possible to estimate it accurately, being upwards of 70,000 ohms. Various rubber membranes tested in this manner gave results of the same order of magnitude. When the same experiment was performed, using a parchment membrane, the edges of which protruded so that they did not dip into the brine, the resistance measured was less than an ohm. Using the same arrangement with a rubber membrane and a normal solution of silver nitrate in pyridine as the liquid on each side, the resistance was over 90,000 ohms, and remained the same for four days, when the experiment was discontinued. A small hole pricked through the membrane with a needle in the latter case caused the resistance to drop to 450 ohms.

jar it thoroughly without, however, upsetting it or otherwise modifying it in any way. Some minutes later when I chanced to look at the apparatus, I noticed that the level of the mercury, which had been practically constant, had risen over 2 cm. higher. The apparatus was then shaken repeatedly from time to time, seizing it with an insulating cloth so as not to alter the temperature, with the result that each time the pressure rose somewhat higher. The 'explanation' of this was, of course, perfectly obvious at once. The pressure is produced by the entrance of solvent into the osmotic cell, consequently right on the inner side of the membrane the solution becomes more dilute than at other points in the interior of the cell. If the cell is left undisturbed the very slow processes of diffusion seek to equalize the strength of the solution in the cell, but clearly shaking the apparatus, or, better yet, stirring the interior content of the cell, would at once accomplish what it would take diffusion processes a very long time to do, even though they be aided somewhat by gravity, owing to the form of the osmotic cell. And it was moreover perfectly evident, too, that to shake the osmometer, filled as it was with considerable pressure on, would not thoroughly mix the contents of the osmotic cell. It is clear that with a more dilute solution in immediate contact with the inner side of the membrane than is in the rest of the osmotic cell the maximum osmotic pressure can not be attained. Furthermore, as in cells slightly different in form when left perfectly at rest the dilute layer in contact with the inner side of the membrane would in general not disappear at the same rate by diffusion and disturbances due to gravity and difference of density of the layers, concordant results could not be expected in duplicate experiments, however carefully performed, without stirring the contents of the osmotic cell. *In all direct measurements of osmotic pressures which have for their aim the determination of the maximum pressure attainable in a given case, it is consequently necessary to stir the interior contents of the osmotic cell continually while the measurement*

is being made, in order that the concentration of the contents of the cell may remain uniform and a layer of maximum concentration be kept in immediate contact with the inner side of the septum. Again, since there really is no such thing as a semi-permeable membrane in the strict sense of the word—which fact has already been emphasized above—it is evident that some of the inner content of the cell, be it ever so slight, is making its way through the membrane into the outer liquid. Thus right next to the membrane on the side bathed by the outer liquid, the septum is really not in contact with the pure solvent—the outer liquid—but rather with a *solution* more or less dilute. When the apparatus is at rest, the slow diffusion processes, aided by gravity perchance, tend to keep the outer liquid of uniform concentration; but these agencies clearly can not be relied upon to keep pure solvent in contact with the outer surface of the membrane in osmotic pressure measurements. Indeed, when the surface of the membrane is not smooth and presents considerable area to the outer liquid, a film of liquid is apt to adhere tenaciously to the outer surface of the septum, in spite of the effects of diffusion. In the usual osmotic experiments using aqueous sugar solutions in a cell made by precipitating copper ferrocyanide on the inner side of an unglazed porcelain cup, the slight amount of sugar that passes through very likely lingers very tenaciously in the pores of the cup just outside of the actual membrane, forming there a film of solution of such strength that its effect upon the osmotic pressure is not a negligible quantity. At least its effect can not be assumed to be negligible without further experimental work. Nor would stirring the outer liquid in such a case as this be apt to remove the difficulty. In the osmotic cells described above where thin rubber membranes supported by cloth and perforated steel discs were used, the effect in question is no doubt less than in the walls of a porous cup, but it is by no means negligible. Here the cloth and the disc hinder diffusion, and it is very necessary to stir the outer liquid thoroughly

and continuously in making the osmotic pressure measurements.

I would like to emphasize here once more then that it is very essential to stir the contents of the osmotic cell and also the outer liquid continuously in any attempt to measure directly the maximum osmotic pressure that may be produced in a given case; and that since in all past experiments this has been entirely neglected, the results of such experiments can not be considered as final and conclusive. In reality, as has been pointed out above in connection with the ether, water, chloroform experiment of L'Hermite, the membrane itself ought also to be stirred during the process. This is of course less necessary when the septum is quite thin than when it is thick. It should be borne in mind, however, that even stirring the contents of the cell and the outer liquid simultaneously can never entirely keep the concentration of the liquid layers in immediate contact with the two sides of the septum exactly the same as the concentration of the liquids further away from the membrane; yet in many cases this may be accomplished with a fair degree of approximation. Moreover, by using the stirring process, the osmotic pressures may be measured fairly approximately even when the amount of material passing out of the cell is not negligible; in other words, when the membrane is not semipermeable.

The apparatus devised for stirring the contents of the cell and also the outer liquid simultaneously during the measurement of osmotic pressures is pictured in Fig. 7 in diagrammatic form. In the figure, the beaker B of a capacity of 1000 cc or more, contains the outer liquid. The latter is stirred by means of the stirrer F, which is moved up and down by the motion of the crank C. In the experiments performed it was admissible to make this stirrer of iron, for this is not attacked by pyridine. F consisted then of a bright, stout iron wire bent in ring form. Just above the cork closing the beaker, this stirrer F was jointed so that it would not need

so large an opening in the cork in which to move up and down. A thermometer is placed in the liquid to register the temperature. The whole apparatus is set in a constant temperature room, or the beaker B is immersed in a bath of constant temperature, not shown in the figure. The osmotic cell S is made exactly as heretofore described, except that before tying on the membrane, the stirrer is inserted into the apparatus through the opening in the bell of the thistle tube. This stirrer consists of a perforated disc of light sheet iron fastened by riveting and a drop of solder, to a sufficiently stout, yet flexible, iron wire, the upper end of which carries a lug of soft iron soldered on, as shown in the figure. In order that the perforated disc at the lower end of this stirrer might not pound on the delicate membrane and injure it, prongs of wire were soldered on the main vertical wire of the stirrer; and after the latter had been introduced into the osmotic cell, these prongs were bent outward in such a way that they would strike the side of the bell of the thistle tube (see figure) as the stirrer moved downward, thus allowing the perforated disc to come close to the membrane without actually touching it. These prongs, of course, do not interfere with the upward movement of the stirrer. The soft iron lug at the upper end of the stirrer had a longitudinal groove (not shown in the figure) filed into it to facilitate the introduction of the liquid into the cell. After the glass part of the osmotic cell had been blown in one piece, the iron stirrer was introduced and the prongs bent into the required position; the membrane was then tied on and supported with cloth and steel disc as heretofore described. The proper quantity of mercury was then introduced and finally the cell was filled with the solution. A fine long funnel tube was employed in introducing the mercury and the solution into the osmotic cell. The upper end of the osmotic cell, through which the cell had been filled, was then drawn off before a blowpipe flame, as already described, so that practically no air remained in the cell after it was sealed. The osmotic cell was

mounted in the beaker as indicated in Fig. 7, the cork closing the cell securely, leaving only a little play for the stirrer F.

Over the sealed end of the osmotic cell is placed the solenoid M; and by making and breaking the current in M, the stirrer in the osmotic cell is moved up and down. By means of the wires LL the small electric motor G is connected with a number of storage batteries; the latter are not shown in the figure. The motor G turns the wheel W, through the agency of a belt, and thus operates the crank C which moves the stirrer F. Now the wheel W is made of hard rubber and on it are fastened two small brass plates PP which are connected with each other by a wire; mounted on separate supports, independent of the wheel W, are the two brass brushes DD, which make contact with PP. These brushes DD are connected with the source of current and the solenoid M by means of wires as shown in the figure. As the wheel W turns and the brushes DD come into contact with the brass plates PP on the wheel, the current in the solenoid M is established, the soft iron lug is attracted and the stirrer in the osmotic cell moved upward only to be dropped again as soon as W has turned far enough to destroy the electrical connection.[1] Thus both the outer liquid and that in the cell are stirred continuously. R is a resistance to regulate the current in the solenoid. It was found that in order to get good steady motion the hard rubber wheel W was too light. This defect was remedied by boring holes A through the wheel near its edge all around the circumference, and filling these with lead. On the same axis with W was another wheel (not represented in the figure) of the same size and weight, which served to balance the apparatus and at the same time to operate the stirrers of a second osmotic experiment like that shown in the figure. Thus osmotic experiments could be performed in

[1] The arrangement was such that the slight heating effect produced by the current in passing through the solenoid was negligible, for the readings of the manometer did not change perceptibly after the current had been turned off and sufficient time allowed for any difference in temperature to become equalized.

duplicate, using but one motor. The arrangement for making and breaking the current in the solenoids of course did not require duplication, since the same current could be sent through both coils in series.

With this new apparatus the osmotic pressures of 0.125 normal LiCl solution in pyridine and also of 0.125 solution of cane sugar in pyridine were measured, using vulcanized caoutchouc as the membrane and pure pyridine as the outer liquid. The 0.125 normal solutions were selected rather than the 0.25 normal, because the latter yielded a rather higher pressure than could be conveniently estimated with an open manometer. The preliminary results (above recorded) obtained with 0.25 normal sugar solutions without shaking do not indicate this, for the highest pressure observed was below 200 cm; but it was found that by stirring, this pressure could be about doubled.

With the stirring apparatus described, Fig. 7, it, of course, takes much more time to set up each individual experiment, for the arrangement is much more complicated. The necessity of stirring in osmotic experiments was only found out after a long series of preliminary tests made in the old-fashioned way without stirring, and so during the time left only a limited number of tests could be carried out. Working with pyridine, moreover, has a very depressing effect on the nervous system, it being impossible to keep the air in the laboratory entirely free from it. The effect appears to be cumulative in character, for one's system seems to become more and more sensitive to the substance. For this reason I felt constrained not to prolong the work with pyridine unduly. It will be remembered that I have carried on experiments with pyridine continuously for about two years, and off and on for a much longer time. During the investigations I have at times found it necessary to counteract the depressing effects of pyridine by taking small doses of strychnine.

The results of the experiments performed with the stirring apparatus will now be given. It need hardly be stated again

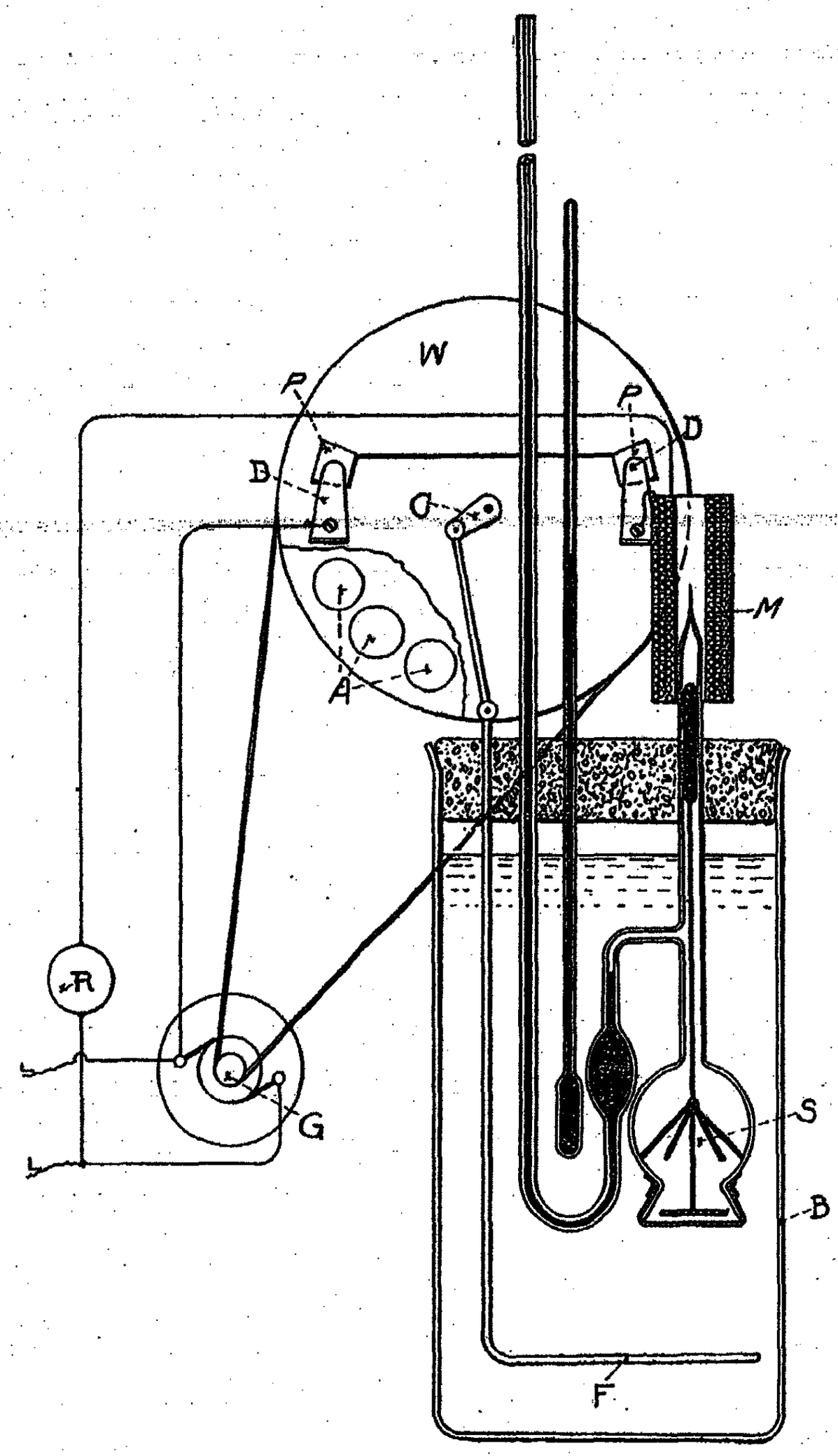


Fig. 7

that the LiCl and the sugar were dry and of a high degree of purity, as was also the pyridine.

57. The inner liquid was 0.125 normal solution of LiCl in pyridine and the outer liquid pure pyridine. It required 46 cc to fill the cell. The volume of the outer liquid was 600 cc. The temperature was 19°.0, and the experiment was run for three days with constant stirring. The maximum height which the mercury column reached was 51.2 cm at 19°.0 C, corrected. This height was practically attained during the first twenty-four hours. At the end of the experiment, the whole of the outer liquid was evaporated to dryness and the LiCl in the residue estimated. It was found that the 600 cc of outer liquid contained 0.0130 gram of LiCl, which shows definitely to what extent the solute has actually passed into the outer liquid.

In the light of what has been said in the preceding pages, it is evident that a determination of the exact amount of solute present in the outer liquid at the time when the maximum pressure is attained is an essential part of all final osmotic pressure measurements, yet such estimations have hitherto always been omitted even in experiments in which great care has been bestowed upon other details.

58. This experiment was exactly like the preceding one (No. 57) except that the outer liquid consisted of 1200 cc of pyridine instead of 600 cc and the temperatures were as indicated below. The experiment was continued for twenty-seven days, at the end of which time an examination showed the membrane to be perfectly intact. The entire outer liquid was finally evaporated to dryness and the LiCl determined in the residue. It was found that the 1200 cc of the liquid contained but 0.0267 gram of LiCl. The pressure rose slowly, the mercury column measuring over 50 cm after the first day. On the sixth day the mercury column measured 51.5 cm, the temperature being 24°.0. On the twelfth day the mercury column measured 53.2 cm, the temperature being 20°.95; on the fourteenth day, 54.9 cm, the temperature

being 21°.96; on the fifteenth day 54.2 cm, the temperature being 19°.6. The beaker containing the outer liquid was then packed in melting ice. The temperature sank to 2°.0 and was kept there for twelve hours. After two hours of thus cooling, the mercury column was only 9.0 cm high and remained there without change for the remaining ten hours. The ice was allowed to melt gradually for the next twelve hours. When the temperature had reached 21°.4 C the mercury column measured 56.1 cm; this was on the seventeenth day. During the next three days the outer beaker was again kept surrounded with melting ice. It was difficult to keep the temperature of the apparatus perfectly constant during all this time. It gradually sank to 2°.2 and finally to 1°.6. When the temperature had reached 1°.6 the pressure indicated by the manometer was 2.9 cm and remained constant for six hours. The temperature was then gradually raised, and at 20°.5 the mercury column reached a height of 53.0 cm, where it remained constant for twelve hours. The outer beaker was then surrounded with a bath of a temperature of 36° C, the change to that temperature being made gradually, which, of course, was also done in the preceding cases where the temperature of the bath was radically altered. At 36° the height of the mercury column became constant at 101.0 cm and remained so for about half a day, when the temperature of the bath was gradually raised to 58°.7 and kept there. At this temperature the mercury column rose to a height of 128.3 cm, where it remained practically constant for two hours. The temperature was then gradually permitted to fall, and at 25°.5 C the column in the manometer finally registered 51.9 cm on the last day of the experiment. It was after all this that the entire outer liquid was evaporated to dryness and the amount of LiCl in the residue determined with the result already recorded. The discussion of the results of this experiment will be deferred until after the next two experiments have been described.

59. The inner liquid was a solution of sugar in pyridine

containing 0.125 gram-molecule per liter. The outer liquid was pure pyridine and the septum vulcanized caoutchouc. The experiment was run with constant stirring for three days, the temperature being kept constant at 20° C. The maximum pressure reached was 98.3 cm, nearly the whole of which was attained during the first day. On concluding the experiment the whole of the outer liquid consisting of 400 cc was evaporated to dryness; the residue was taken up with water, and the sugar determined with Fehling's solution, after inverting with HCl. It was found that the 400 cc contained 0.1149 gram of sugar.

60. This experiment was as nearly as possible a duplicate of the preceding one (No. 59). On the fifth day the mercury in the manometer reached a height of 91.8 cm, the temperature having gradually gone up to 21° C. In this case too the pressure increased but little after the second day. On the morning of the seventh day the pressure was 94.0 cm, the temperature being 21°.95 C; in the evening of the same day 95.5 cm at 22°.15. On the eighth day the outer beaker was packed in melting ice, the temperature in the beaker being 2°.0 C. During this time the mercury in the manometer registered practically no pressure, or at best only a few millimeters. The ice was then permitted to melt gradually, and on the ninth day the pressure registered 92.0 cm at 19°.4 C. The temperature was then slowly raised to 46° C, where it was kept for twelve hours. The pressure became constant after about three hours at 114.2 cm and remained there for nine hours. The experiment was then discontinued. The whole of the outer liquid consisting of 1200 cc was then evaporated to dryness, and the sugar was taken up with water, inverted with HCl and determined with Fehling's solution. The result was that in the 1200 cc 0.2205 gram of cane sugar was found.

Taking into consideration the pressures developed while the apparatus is kept nearly at a constant temperature, we find that according to No. 57 the osmotic pressure of the 0.125

normal solution of LiCl is 51.2 cm at 19°.0, and according to No. 58 it is 54.2 cm at 19°.6. Again, according to No. 59 the osmotic pressure of a 0.125 normal sugar solution is 98.3 cm at 20°.0, while according to No. 60 it is 91.8 cm at 21°.0. Even in these cases the agreement of the duplicates leaves much to be desired, for the differences in pressure observed can hardly be due to the slight differences in temperature. They are more likely due to individual differences in the membranes used, and to the fact that even with constant stirring, it was not quite possible to keep the liquids in immediate contact with the membrane of perfectly uniform concentration on each side. These difficulties have already been discussed at length above. There can be no doubt, however, that the results obtained are approximately the osmotic pressures of the solutions in question, under the conditions of the experiments.

The effect of stirring is clearly shown by a comparison of experiment No. 54 where the highest osmotic pressure of a 0.125 normal sugar solution was found to be 62.4 cm at 17°.5 without stirring, and the result recorded in No. 59, where with stirring the osmotic pressure was found to be 98.3 cm at 20°.0.

Taking the highest values found, namely 54.2 cm for 0.125 normal LiCl solution at 19°.6 and 98.3 cm for 0.125 normal sugar solution at 20°.0, we note (1) *that the electrolyte gives by far the lower pressure*, and (2) that neither the LiCl nor the sugar give anywhere near the pressure called for by the gas laws, according to which a 0.125 normal sugar solution ought to give a pressure of approximately three atmospheres (228 cm Hg) at 20°. Further, it will be recalled that a 1.2 percent solution of sugar yielded practically no osmotic pressure at 0°, whereas according to the gas laws it ought to have produced about 0.8 of an atmosphere. And again, 0.05 normal solution of $AgNO_3$ yielded no osmotic pressure, whereas according to the gas laws it ought to have produced over an atmosphere. Further, the changes of pressure above recorded as caused by changes of temperature are so very

much greater than they would be if they were proportional to the absolute temperature that additional comment seems quite superfluous. The osmotic pressures here investigated, then, do not follow the gas laws at all. Again, the electrolyte LiCl yields a much lower pressure than the non-electrolyte, sugar, which is exactly the opposite of what the theory of electrolytic dissociation requires.

Observations Concerning Dialysis

When both cane sugar and copper oleate are dissolved together in pyridine and the solution is separated from pure pyridine by means of a vulcanized caoutchouc membrane, the copper oleate passes through the septum and the sugar remains behind. This is what one would expect from what has been said above. But here we have a case where a crystalline body, the sugar, is separated from a non-crystalline substance, the copper oleate, by dialysis in which process the non-crystalline or colloid body passes through the septum and the crystalloid remains behind. Again, when camphor and sugar are together dissolved in pyridine and the solution is separated from the solvent by means of a rubber septum, the camphor passes through and the sugar remains behind, which might have been anticipated. Here we have a case in which crystalloids are separated from each other by dialysis.

In fact it is clear that in general any substance which is soluble in both hydrocarbons and in pyridine may be separated from sugar by dialysis, when the pyridine solution of it and the sugar is separated from the pure solvent by a rubber septum. In such cases the sugar will always remain behind in the dialyzer and the other substance will pass through whether it be crystalline or non-crystalline. Any other substance soluble in pyridine but not soluble in hydrocarbons, may in general be substituted for sugar. Thus the rôle of the nature of the membrane in the process of dialysis is demonstrated. The current view that crystalloids always pass through membranes more readily than colloids is evidently untenable, it has been shown that just the opposite may occur,

and that even crystalloids may be separated from each other by dialysis when the proper septum is chosen. *Whether substances can be separated by dialysis or not does not depend at all upon their crystalline or non-crystalline nature as is so commonly supposed, but upon their affinity for the septum employed.* After what has been said above, it is evident that stirring the liquids hastens dialysis.[1]

Several experiments in addition to those here described have been performed, but as I hope to continue the experimental work on dialysis their presentation will be reserved for a later communication.

General Remarks

The conclusion reached above that the process of osmosis depends upon selective solubility (in other words, upon the affinities involved) is in agreement with what Overton[2] has found in his physiological studies. The importance of the recognition of the true nature of osmotic processes for progress in physiology can hardly be overestimated.

From the time of Dutrochet all investigators who worked on osmosis experimentally with different membranes and various liquids have been impressed with the important rôle of the nature of the membrane in determining whether osmosis would occur at all or not, and if so, in what direction. The following quotation taken from the article of L'Hermite, cited above, shows how clearly he had grasped the situation: "Je pense avoir démontré par la discussion des expériences de mes devanciers et des miennes, que l'endosmose n'est point le resultat d'une force particulière, mais de l'affinité elle-même en étendant l'acceptation de ce mot a l'attraction capillaire qui en est le premier degré." I should also like to quote the opinion of Raoult, which he voiced in a letter written

[1] Since the above was written it came to my notice that in 1848 Jolly, Liebig's Ann., 68, 6 (1848), refers to a case where he shook the dialyzer to hasten the process.

[2] Vierteljahrsschr. d. naturforsch. Ges. in Zürich, 44, 88 (1899). See also the discussion in Chap. 5 of Höber's Physik. Chem. d. Zelle u. Gewebe, Leipzig (1902). Compare also Livingston, "The Rôle of Diffusion and Osmotic Pressure in Plants," Chicago (1903).

January 7, 1897, to Prof. W. D. Bancroft, and which through the latter's kindness I am able to present here. This quotation, which requires no further comment, gives everything contained in the letter relative to the osmotic process.

"La question de l'osmose, que beaucoup croient résolue par des formules mathématiques fondées sur des hypothèses commence à peine à être posée. Mes expériences auxquelles vous faites allusion, prouvent qu'i ly a certainement des diaphragmes *actifs*. Existe-t-il également des diaphragmes *passifs*, comme pour les gaz? Pour le moment tout le mond paraît le croire, sur la foi de van't Hoff; mais pour mon compte, je n'en ai jamais pu trouver un seul.

"Si je n'ai pas continué mes publications sur ce suject, c'est que j'ai rencontré de très grandes difficultés pour mesurer les pressions osmotiques avec des diaphragmes mous. Existe-t-il, d'ailleurs, une veritable pression osmotique? Je n'en suis pas sûr. Il arrive certainement toujours une pression pour laquelle le mouvement osmotique semble s'arrêter; mais j'ai lieu de croire qu'elle correspond au moment où la quantité de liquide qui passe dans un sens par *osmose*, est égale à celle qui passe en sens opposé par *filtration*.

"La question est intéressante et fort délicate. Aussi, verrais-je avec un très grand plaisir d'autres expérimentateurs s'engager dans cette voie."

Again, very recently Barlow[1] working in the laboratory of J. J. Thomson has re-emphasized the fact that the osmotic current is caused by the mutual potential energy of solution of the liquids and that the direction of osmosis is conditioned by the character of the membrane.

Precipitated membranes, like those of copper ferrocyanide, etc., are hydrates, that is, they contain more or less water. When such a membrane is used to separate water from an aqueous solution, the latter abstracts water from the septum—the hydrate—which again takes up water from the side bathed by the pure solvent. The affinity of the solution

[1] l. c.

for additional solvent must be sufficient to extract some water from the membrane in order that an osmotic pressure may be produced. If in addition the solute has considerable affinity for the septum, copper ferrocyanide for example, as many of the salts of the alkali metals are known to have, for instance, the solute will pass through to a notable extent; if on the other hand, the solute has very little affinity for the septum, as is the case with cane sugar, the membrane will allow but very small quantities to pass through, and hence will be "semipermeable." It is perfectly clear, too, that, in general, different precipitated membranes would lose part of their water with different degrees of readiness, and hence in quantitative measurements of osmotic pressures different results would be obtained when different precipitated membranes are used. This is shown to be true by the experiments of Pfeffer[1] who found that when a copper ferrocyanide membrane was used a 1 percent sugar solution yielded an osmotic pressure of 51.0 cm at 14°.2; when a Prussian blue septum was employed the pressure was 38.7 cm at 13°.9; and when a calcium phosphate membrane was used the pressure was 36.1 cm at 15°.2. In all three cases the sugar which passed through the septa was insignificant according to his determinations. While the results of Pfeffer are not final as determinations of the maximum osmotic pressures, inasmuch as he did not stir the liquids while measuring the pressures, the experiments nevertheless serve to show that the pressures developed with the different septa are by no means the same. If one were to compute the molecular weight of sugar from the osmotic pressures which a 1 percent aqueous solution of it develops when copper ferrocyanide, Prussian blue and calcium phosphate are used as membranes respectively, different values would obviously be obtained, that is, the conclusion would be reached that the molecular weight of sugar in one and the same solution varies in different cases, which is obviously absurd. The experimental facts

[1] "Osmotische Untersuchungen."

are, of course, readily explained by what has been said above.

Further, when precipitated membranes are used and the osmotic process goes on very rapidly, it generally occurs that the solution robs the precipitated hydrate of water faster than the latter is taken up from the pure water bathing the other side of the septum. In such cases the membrane develops ruptures through which the solution oozes out of the cell, hence the necessity of the usual practice of adding the "membrane formers" to the liquids on each side of the membrane to repair such leaks. It is obvious that in any osmotic experiment the composition of the septum is always in a state of change, though the extent of this may be slight in some cases. Here lies one of the chief difficulties of measuring osmotic pressures (which are equilibrium pressures) with soft diaphragms to which Raoult alludes.

It must be borne in mind that the application of the gas laws, either in simple or modified form, to dilute solutions is based upon the experiments which Pfeffer made with copper ferrocyanide membranes, and which Morse and Frazer have recently sought to verify. But these experiments have all been made without stirring and with but one membrane, and hence are not final. Furthermore, the osmotic pressures of sugar solutions in pyridine, using vulcanized caoutchouc as the semipermeable membrane, show definitely that the gas laws do not obtain here at all. In the face of the experimental facts which we now have as showing the nature of the osmotic process and the magnitude of the osmotic pressures under different conditions, the general, indiscriminate application of the gas laws in their simple or somewhat modified form to all dilute solutions, and even to some that are not dilute, as now in vogue, can not be too greatly deplored. To speak of the osmotic pressure of any isolated solution without specifying what membrane separates it from what other liquid is nonsense,[1] in the light of the facts here presented. And further, to assume that solutes are polymerized

[1] Compare also views expressed by Van Laar, Chemisch Weekblad, 2, 1–16 (1905).

or dissociated in dilute solutions because the osmotic pressures developed by the latter in given cases happen to deviate from values computed from the gas laws is evidently equally unjustifiable practice.

Summary

In this paper it has been shown that whether osmosis will take place in a given case or not depends upon the specific nature of the septum and the liquids that bathe it; and if osmosis does occur, these factors also determine the direction of the main current and the magnitude of the pressure developed. The motive force in osmotic processes lies in the specific attractions or affinities between the liquids used, and also those between the latter and the septum employed. These attractions or affinities have also at times been termed the potential energy of solution, etc., they are to the mind of the writer essentially the same as what is commonly termed chemical affinity.

It has been emphasized that osmotic pressures are equilibrium pressures, and that in osmotic processes there is always a current in both directions, though the main current may in specific cases be so much stronger than the minor that the latter almost sinks into insignificance. In such cases the septum employed is termed "semipermeable."

Vulcanized caoutchouc has been found to be a "semipermeable" membrane when it separates pyridine solutions of silver nitrate, lithium chloride, and cane sugar from the pure solvent.

The necessity of stirring the contents of the osmotic cell and also the outer liquid during osmotic pressure measurements has been pointed out, and a new apparatus for measuring osmotic pressures accordingly has been devised.

The results of the osmotic pressure measurements show that the gas laws do not hold; and it has consequently been pointed out that the latter cannot serve as a basis for a satisfactory theory of solutions.

The advantage of stirring in processes of dialysis has been indicated; and it has been shown that whether substances pass through membranes or not does not depend upon their colloidal or crystalloidal character, but solely upon their affinity for the membrane employed and for the liquids that bathe it.

In conclusion I desire to thank Messrs. F. L. Shinn, J. H. Mathews, Wm. Marquette and H. E. Eggers for assistance which they have kindly rendered me from time to time in the experimental part of the work.

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THE SOLUBILITY OF GYPSUM IN MAGNESIUM SULPHATE SOLUTIONS[1]

BY F. K. CAMERON AND J. M. BELL

The solubility of gypsum in aqueous solutions of magnesium sulphate has not been studied systematically and the few results recorded in the literature must be considered as of a qualitative nature only. Fassbender[2] states that no gypsum dissolves in a saturated solution of magnesium sulphate even after several days' contact. Droeze[3] has repeated the experiment at 13.5° and by analysis of the residual solid finds all the calcium sulphate which was originally added. The solubility of gypsum in a solution of magnesium sulphate one-tenth saturated, he gives as 0.86 gram per liter.

There is no accurate method of separation of small amounts of calcium from large amounts of magnesium. The separation of calcium from magnesium by precipitation with ammonium oxalate is feasible only in case the magnesium salts are present in small amount. This is due to the well-known solvent action on calcium oxalate by magnesium salts. The method based on the solubility of magnesium sulphate in aqueous alcohol and the insolubility of calcium sulphate in this solvent is not delicate enough to estimate the calcium in solution when the concentration of magnesium sulphate is great. Attempts to determine the composition of such solutions by analytical means were therefore abandoned and a different method was resorted to.

As the detection of small quantities of calcium in the presence of large amounts of magnesium is not feasible in a wet way, the magnesium sulphate was examined spectroscopically and no calcium could be discovered. As a large

[1] Published by permission of the Secretary of Agriculture.

[2] Ber. chem. Ges., 9, 1358 (1876).

[3] Ibid., 10, 330 (1877).

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quantity of magnesium might, however, mask the presence of traces of calcium, a trace of lime salt was added to a concentrated solution of the magnesium sulphate and this solution was examined spectroscopically. The calcium lines were quite distinct. It was calculated that the ratio of calcium to magnesium in this solution was about one to seven hundred, and hence the amount of calcium originally present must at least have been very much less.

Definite quantities of a concentrated solution of magnesium sulphate of which the composition had been determined were diluted with definite amounts of water, the whole volume of each solution being about 200 cc. These solutions, 18 in all, varying in composition from pure water to a solution almost saturated, were contained in salt-mouth bottles of 200 cc content. A glass rod passed through the paraffined cork, and almost touched the bottom of the bottle. To the lower end of the rod a weighed plate of pure selenite ($CaSO_4.2H_2O$) was attached by means of rubber bands, and after fitting the cork tightly into the bottle the whole top was paraffined over. The bottle was then rotated in a horizontal position around its axis. The temperature of the thermostat varied at most 0.1° from 25° C. After two weeks the bottle was opened and the crystal of selenite was drained, washed with 50 percent alcohol, dried and weighed. This procedure was then repeated at intervals of one week until the selenite plate had assumed a constant weight. In most cases the crystal had reached constant weight after four weeks, but in some cases not until five weeks had elapsed.

As soon as equilibrium had been attained the density of each solution was determined. Thus, both mass-concentration and volume-concentration may be computed. In the case of the solution saturated with respect to both gypsum and $MgSO_4.7H_2O$, the volume of solution was determined by removing the solution from the crystals of magnesium sulphate by suction. This solution was also analyzed for mag-

nesium, the content of $CaSO_4$ being known from the decrease in the weight of the selenite plate. From these data and the density; the volume concentration of the solution has been computed.

The results are given in the following table, and have been plotted in the accompanying diagram.

SOLUBILITY OF GYPSUM IN MAGNESIUM SULPHATE SOLUTION AT 25° C

Density $\frac{25°}{25°}$	$MgSO_4$ per liter	$CaSO_4$ per liter
1.0032	0.0	2.046
1.0055	3.20	1.620
1.0090	6.39	1.507
1.0118	10.64	1.471
1.0226	21.36	1.478
1.0419	42.68	1.558
1.0626	64.14	1.608
1.0833	85.67	1.617
1.1190	128.28	1.627
1.1377	149.67	1.597
1.1479	165.7	1.549
1.1537	171.2	1.474
1.1813	198.8	1.422
1.2095	232.1	1.254
1.2382	265.6	1.070
1.2624	298.0	0.860
1.2877	330.6	0.647
1.3023	355.0[1]	0.501

The data concerning the concentration of the solution in equilibrium with both gypsum and magnesium sulphate, agree well with those determinations by Basch.[2] From the above table the content of this solution in magnesium sulphate is 26.8 percent, and from the work of Basch at 25°, it is calculated as 27.2 percent.

[1] Saturated with $MgSO_4.7H_2O$.

[2] Künstliche Darstellung und Bildungsverhältnisse des Polyhalits, Inaug.-Diss., Berlin, 1901. The data have been given in a paper by van't Hoff: Zeit. anorg. Chem., 47, 244 (1905).

It will be seen from the diagram that the solubility of gypsum is depressed very much by small quantities of magnesium sulphate. The solubility curve has a minimum point at about 13 grams $MgSO_4$ and 1.46 grams $CaSO_4$ per liter. From this concentration the solubility gradually increases for increasing amounts of $MgSO_4$ in the solution to a maximum point at about 105 grams $MgSO_4$ and 1.64 grams $CaSO_4$ per liter. From this point the solubility decreases again with higher concentrations of $MgSO_4$. The solution saturated with both salts has a concentration of 355 grams $MgSO_4$ and 0.50 gram $CaSO_4$ per liter.

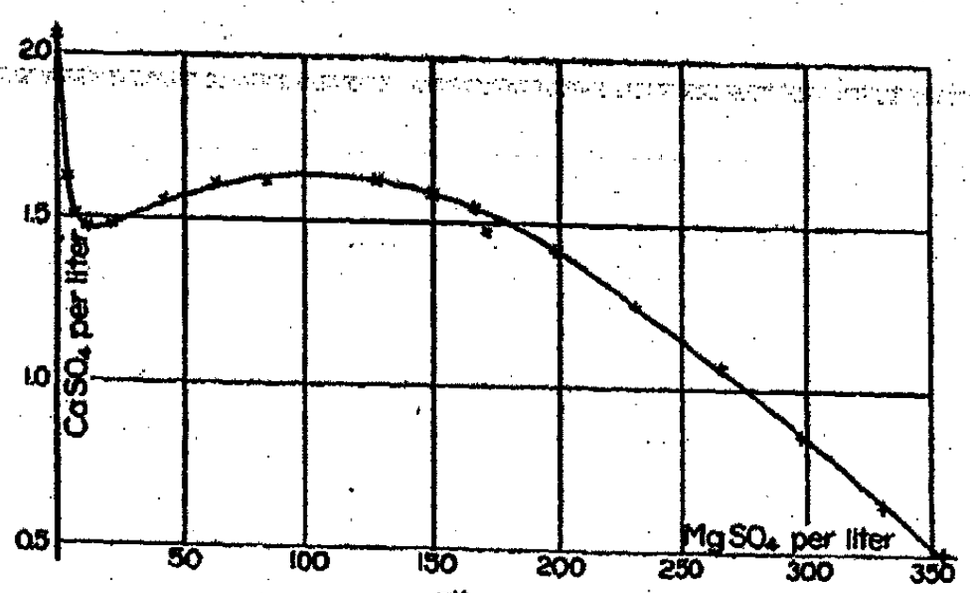


Fig. 1

This is a remarkable solubility curve in that it shows both a minimum and a maximum point. It may be definitely affirmed that this has not been due to any change of solid phase, for had this occurred the gypsum plate would have been decomposed more or less completely to form the new phase, and successive weights of the crystals would have had wide variations in weight.

These results suggest a means of analysis of calcium in the presence of large amounts of magnesium. Convert into sulphates and add a weighed crystal of selenite to a known amount of the solution and agitate as has been described, until the weight of the crystal becomes constant. The solution is then analyzed in the usual way for magnesium. The

solubility of gypsum in a solution of this concentration can be estimated from the chart. The difference between this solubility and the loss of weight of the crystal gives the amount of calcium already present in solution.

The rapid decrease in the solubility of gypsum for small amounts of magnesium sulphate finds a parallel in the depression in solubility due to the other sulphates, sodium,[1] potassium[2] and ammonium,[3] while in the case of sulphuric acid[4] there is almost a constant solubility at 25° up to a concentration of 3 grams H_2SO_4 per liter. Quite different, however, is the effect of salts in the solution which yields no common ion. In every case a slight quantity of such a salt will increase the solubility of gypsum over that in pure water. It seems probable, therefore, that this depression in solubility is due to the effect of the common ion.

Two tentative suggestions are offered in explanation of the minimum point and the maximum point. The first suggestion is that the peculiar shape of the curve may be due to changes in the density of the solvent. There is no method, so far as we know, of determining what the density of the solvent is under any circumstances, but it is well-known that such changes occur. In some cases the volume of the solution is less than the volume of the pure solvent and there can be no doubt that a change in density has occurred. The second tentative suggestion is based on the effect of the dissociation upon the solute, by attributing specific effects on the different materials in solution. From the point of view of the dissociation hypothesis magnesium sulphate in solution forms the magnesion and the sulphion. Assuming that these ions tend to change the solubility in opposite directions, the sulphion to depress it and the magnesion to increase it, there may come a concentration at which the

[1] Cameron and Seidell: Jour. Phys. Chem., 5, 643 (1901); Cameron and Breazeale: Ibid., 8, 335 (1904).

[2] Cameron and Breazeale: Ibid., 8, 335 (1904).

[3] Sullivan: Jour. Am. Chem. Soc., 27, 529 (1905).

[4] Cameron and Breazeale: Jour. Phys. Chem., 7, 571 (1903).

solvent action of the magnesion overcomes the depressing action of the sulphion and the solubility increases. At higher concentrations the amount of undissociated salt becomes great relatively to the ionic concentrations, and assuming that this depresses the solubility the amount of gypsum going into solution will diminish with increasing amounts of magnesium sulphate. This point of view of the specific solvent action of ions is supported by a consideration of the solvent action upon gypsum of various nitrates and chlorides in solution. For equimolecular quantities of the chlorides of hydrogen, magnesium, ammonium, sodium and potassium where the concentration is quite low and consequently ionization almost complete the solvent capacity of these chlorides is greatest for HCl and so on in the order named for the temperature 25°. Thus by keeping the effect of the chlorine ion practically constant the difference in solvent action of the various cations may be estimated. In the case of the nitrates, by holding the effect of the anion constant, the solvent capacity of the cations is found to be in the same order as in the case of the chlorides. The hydrogen ion has by far the greatest solvent action, then magnesium, then ammonium, sodium and potassium, the solubility curves for the last three lying quite close together. It is interesting to note that the solvent action of the cations decreases with increase in the combining weight of the ion.

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ON THE RELATION BETWEEN ELECTROLYTIC CONDUCTION, SPECIFIC INDUCTIVE CAPACITY AND CHEMICAL ACTIVITY OF CERTAIN LIQUIDS

A CORRECTION

BY JOSEPH HOWARD MATHEWS

Dr. Herman Schlundt has kindly called attention to certain typographical errors which appear in my recent paper[1] bearing the above title. The errors referred to occur in the last column of Table VIII, page 665, and are the result, apparently, of a downward shift of the type of the last five lines. Here the table should read as follows:

Substance	Maker	D. C.	Resonance	Temp.	B. P.	Remarks
Diethylamine	Schuchardt	3.7	Good	23°	—	Schlundt, 3.58
Dibenzylamine	"	3.6	"	23°	—	" 3.55
Diphenylmethane	Trommsdorf	2.5	"	18°	243°–44	
		2.45		18°	245°	New sample
Dipropylamine	Schuchardt	2.9	"	18°	110?	Schlundt, 2.9
Dimethylaniline	"	5.0	"	18°	189.5–90	" 5.07

Thus it will be seen, as it was my purpose to show, that our results are satisfactorily concordant. Dr. Schlundt has also called attention to the fact that for tin-tetrachloride he obtained the value 3.20. On page 658 it will be noted that I obtained precisely the same value as was obtained by Schlundt. The value 2.0 given in the table is not correct.

I wish to thank Dr. Schlundt for his kindness in calling attention to these errors.

Laboratory of Physical Chemistry,
Harvard College, December, 1905.

[1] Jour. Phys. Chem., 9, 641 (1905).

NEW BOOKS

The Elements of Physical Chemistry. *By J. Livingston R. Morgan. Third edition, revised and enlarged. 12 × 19 cm; pp. xii + 510. New York: John Wiley and Sons, 1905. Price: cloth, $3.00.*—Dr. Morgan's "Elements" is a small volume of five hundred pages, in which the author has managed to give a "comprehensive outline" of the "whole subject" of Physical Chemistry.

After an introduction, the work is divided into eight chapters, on gases, liquids, solids, the phase rule, solutions, thermochemistry, chemical change (equilibrium, kinetics, applications), and electrochemistry (migration, conductivity, electromotive force), respectively. These are followed by 189 numerical problems with answers, eight tables of data, and an account of Morse and Frazer's experiments on the osmotic pressure of sugar solutions, printed as an appendix.

As this is the third edition, and as in preparing it the author had the benefit of suggestions from the hand of Professor Ostwald, errors in matters of fact are hardly to be looked for. The statement that "up to the present no reactions of an order higher than the third have been found" (page 277) is, nevertheless, inaccurate; the only other slips noted occur in connection with the discussion of maximum and minimum boiling-points (pp. 120, 160) which ought to be rewritten.

A text-book may, however, present features which worry the student far more than mere misstatements of fact; one of them is inconsistency in details. On page 14, for instance, "formula weight" is stated to be identical with molecular weight, on page 175 it is used for the atomic weight of iodine. At the beginning of Chapter VI, "solution" is defined as a "homogeneous mixture which cannot be separated into its components by mechanical means," while a few pages further on the conditions under which this very separation can be effected by piston and cylinder are discussed in detail. Even such a minor matter as the use of the same letter, *n*, with different meanings in the related formulas of pp. 153, 372, and 416, may prove an obstacle to the beginner.

Confusion may also arise from the introduction of "ions" before "migration," particularly as certain statements on pages 103, 144, 146 might be taken to mean that the ions and the products of electrolysis are identical. The saving clause "when secondary reactions are excluded" will hardly save, as no means of recognizing these "secondary" reactions is provided.

The article on the Mass Law would be improved by explaining at the outset that the law deals only with the composition of solutions (including gaseous mixtures); if this were done, the definition of "active mass" on page 224 would be right as it stands, and the necessity for qualifying it on pages 241 and 261 would be obviated. A further improvement could be effected by, as far as possible, dispensing with the "electrolytic solution pressure," and deducing equation (2), page 409, by the method due to Ostwald; not only would the relation in question be readily and clearly obtained, but the temptation to introduce an error of 22 percent by substituting for it equation (1) of the same page would be avoided, and many "relics of the atomistic hypothesis" could be left out of the language of the chapter.

All these are small matters, which the author, if he thinks it desirable, can easily alter in the fourth edition. It would be more difficult, but well worth the labor, to revise the method of dealing with the fundamental conceptions of

thermodynamics. The definition of energy, page 2, as work, or "anything which can be transformed into work or produced from work," would serve almost equally well as a definition of money, or of a goodconscience. The definition of the "capacity factor," on page 3, and in equation (2), page 6, fits heat capacity, or specific heat, to a nicety; and equation (6) is admirably adapted to the passage of heat from a hot to a cold body. On page 4, however, the student is informed that "for heat energy the capacity factor is called 'entropy,' and throughout the book equation (6) is treated as an expression of the second principle."

Finally, it is very desirable that an explanatory note of some kind should be appended to such calculations as those of page 73 (Crompton's law), and page 414 (osmotic theory of cell); as they stand, the tyro will only see that experimentally verifiable conclusions may be extracted from the most improbable premises by the use of $\int$ and pdv, and will be apt to acquire either too high, or too low, an opinion of thermodynamical reasoning.

It has been worth while to go into these matters in such detail, because in many ways the book is just what is wanted. It is the right size, each topic has its fair share of space, full details of the calculations are given in typical cases, a large number of numerical problems are supplied, and the reader's interest is kept alive by the emphasis laid on the application of physical-chemical theorems to questions of general importance. *W. Lash Miller*

The Electrolytic Dissociation Theory, *with Some of Its Applications: an Elementary Treatise for the Use of Students of Chemistry. By Henry P. Talbot and Arthur A. Blanchard. 15 × 23 cm; pp. iv + 84. New York: The Macmillan Company, 1905. Price: bound, $1.25.*—This is a well-written, interesting, dogmatic, little book, designed to enable students "to comprehend the main facts which are to-day generally accepted as supporting the theory, and to understand its application to important types of chemical change."

The illustrations are apt, the experiments are described in detail, the mathematics are reduced to a little arithmetic clearly put, and there is no thermodynamics at all, no epistemology, nor anything of the sort. It is not too much to say that this is the best little book of its kind on the market.

In one respect it is a very bad kind. There is no scientific impartiality about it; everything that might "complicate" matters by suggesting that all is not well with this best of all possible theories, has been carefully excluded. In short, the book is written in the spirit of the evangelist, not at all in that of the higher critic.

Does not such training fill the ranks of them that shout: "The sun do move!" *W. Lash Miller*

Die Aufgaben der Photochemie. *By R. Luther. Antrittsvorlesung. 17 × 24 cm; pp. 18. Leipzig: Johann Ambrosius Barth, 1905. Price: paper, 80 pfennigs.*—The author estimates that the earth receives two hundred billion horse power from the sun in the form of radiant energy. Of this we are only utilizing three-millionths. The man who can convert radiant energy into mechanical energy will control the world. Turning from this exhilarating but specula-

tive theme, the author discusses photochemical reactions. These are considered as being always oxidation and reduction phenomena. The general statement is made that light never retards a reaction. If the light has any effect, it accelerates the reaction. Since only that light can act which is absorbed, the author concludes that colored substances will in general react more rapidly than colorless ones. At ordinary temperatures in aqueous solutions it is said that all oxidizing and reducing agents which react rapidly have absorption bands in the visible spectrum or in the first portions of the ultra-violet.

Stress is laid very properly on the fact that the effect of light on chemical equilibrium will yield more satisfactory results than the study of reaction velocities. Any equilibrium will be displaced by light if one or more of the reacting substances is colored. We have no way as yet of telling how much the displacement will be. *Wilder D. Bancroft.*

Physical Chemistry; *and Its Applications in Medical and Biological Science. By Alex. Findlay. 16 × 25 cm; pp. 68. New York: Longmans, Green and Co., 1905. Price: 75 cents, net.*—This is a series of lectures to students of medicine and biology. The subject is treated under the headings: diffusion and osmotic pressure; cryoscopic method of determining the osmotic pressure; theory of ionization; some applications of the ionic theory; permeability of membranes and absorption; velocity of reaction and catalysis; colloidal solutions; physical chemistry and serum therapy.

The most interesting chapter is that on permeability and absorption. The author discusses the formation of hydrochloric acid in the stomach, absorption from the intestine, and urine secretion. The reviewer wishes that a reference had been given in regard to the following paragraph. "It has been found that certain animal membranes possess the very important property of being permeable only in one direction. Thus, for example, it has been found that the membrane surrounding an egg will allow water to pass inwards, but not outwards; and it has also been shown that the skin of the frog, while permeable in both directions for potassium ion and chloride ion, is permeable for the sodium ion only from outside to inside." The reviewer finds it very difficult to believe in the existence of a unilateral permeability.

While the author does not actually say so, pp. 40–45, the unfortunate student will certainly get the impression that only ions are toxic. The value of the discussion would have been increased very much if reference had been made to Clark's work on the toxic action of the chloracetic acids.

The price of seventy-five cents for sixty-four pages, mostly introductory, is practically prohibitive. *Wilder D. Bancroft*

Handbuch der anorganischen Chemie. *Herausgegeben von R. Abegg. In vier Bänden, Zweiter Band, zweite Abteilung: Die Elemente der zweiten Gruppe des periodischen Systems. 18 × 25 cm; pp. ix + 700. Leipzig: S. Hirzel, 1905. Price: paper, 24 marks; bound, 26 marks.*—According to the preface this series of volumes is to differ in many ways from other works which have preceded it. The results of physical chemical investigations are to be presented in an easily intelligible form and the relation of these to other inorganic investigations is to be shown. Wherever possible the theoretical relations between chemical phe-

nomena are to be emphasized; instead of a mere enumeration of facts, the significance of these facts is to be pointed out. Attention is to be drawn to problems requiring investigation and to the methods of solving them. In addition, the data are to be considered critically so far as may be.

This is a very interesting program and all people will welcome the appearance of this work. As in the case of all reforms it is inevitable that the editor should go to the other extreme and should give more physical-chemical details than are really necessary. The theory of dilute solutions and Abegg's theory of affinity are given full play and the result is interesting though not always convincing. One must recognize that the fundamental idea is a good one and that it has been carried out as well as one could expect at this time.

This volume includes beryllium, magnesium, calcium, strontium, barium, radium, zinc, cadmium, and mercury. A welcome feature of the book is a critical discussion by Brauner of the atomic weight determinations for each element. There is a pleasing scarcity of mistakes and misprints. On p. 342 there seems to be a confusion between electromotive force and potential difference.

Wilder D. Bancroft

Neure Anschauungen auf dem Gebiete der anorganischen Chemie. (*Die Wissenschaft, Heft 8*). *By A. Werner. 14 × 22 cm; pp. xii + 189. Braunschweig: Friedrich Vieweg und Sohn, 1905. Price: paper, 5 marks; linen, 5.80 marks.*— According to the author's point of view the ordinary theory of valency breaks down completely when one passes from organic to inorganic chemistry. In its stead we have the theory of co-ordination. Instead of valence, affinity is to be taken as the starting-point.

"We consider the atoms as volume units of homogeneous matter which for simplicity are assumed to be spherical. In regard to affinity we make the simple assumption that it is an attracting force acting from the center of the atom uniformly towards all parts of the spherical surface. From this conception of affinity it follows necessarily that separate unit valences do not exist. The valency denotes an empirically found ratio according to which the atoms combine and it is independent of separate valences. It does not depend on the atom alone but on the nature of all the atoms which combine to form a molecule. When two atoms combine, the used-up portion of the affinity distributes itself over a definite circular section of the spherical surfaces of the atoms (surface of union) and varies within wide limits according to the nature of these atoms. We thereby obtain a suitable picture of the varying valence relations of the atoms while the arrangement of the surface of union with reference to the relative values leads without further hypothesis to the configuration in space of the molecule, etc.".

The subject is an interesting one and the author is an authority. He has not the gift of tongues, however, and his book is hard reading. It is difficult to keep the underlying hypothesis always in mind and one is continually brought up short as though skating on rough ice. The value of the book is in the substance and not in the style.

Wilder D. Bancroft

The Theory of Experimental Electricity. *By William Cecil Dampier Whetham. 14 × 22 cm; pp. xi + 334. Cambridge: University Press, 1905. Price: bound 8*

shillings, net.—"The great shift in the chief points of experimental electricity, due to recent development in physical science, has changed the proportion of the various branches of the subject, and has put out of date many of the older standard text-books. To the phenomena of electrolysis, of conduction through gases, and of radio-activity, the physicist will now turn for knowledge newly acquired, for knowledge in the making, and for unsurveyed territory ready and waiting the explorer. The writer has a firm belief in the advantage of giving to university students, even to those who confine themselves to an elementary study of their subjects, some insight into methods of research, together with some idea of recent results, and of unsolved problems ripe for examination. In this way interest is aroused, and natural science is presented in its true light, as a living and growing branch of knowledge—imperfect indeed and incomplete as all human creations must be, but more fascinating by reasons of its very faults and limitations, and the consequent possibility of unexpected and beneficent development."

"In the following pages no attempt has been made to present a complete treatment of the science of electricity. The book is meant to be suggestive rather than exhaustive, to be an impressionist sketch rather than a finished picture. It aims at bringing into prominence those features which strike the writer as essential, without wearying the reader with a mass of unnecessary detail. *An educational work is better too short than too long*; better when in some points leaving curiosity unsatisfied than when attaining an ill-digested completeness. The object of the present undertaking has been to implant a thorough and clear knowledge of those physical principles necessary for an appreciation of the newer parts of the subject. All digressions, though interesting perhaps to the mathematician or experimenter, have been curtailed. The book is meant as an organic structure, each part of which has a definite and inevitable relation with the whole, each section its bearing on the plot of the story. To some extent even a scientific text-book perforce must be a piece of literature and a work of art. Whether that necessity be welcomed or not, nothing is lost by keeping it clearly in mind."

The different chapters of the book are entitled: general principles of electrostatics; some theorems of electrostatics; the dielectric medium; magnetism; the electric current; thermo-electricity; electro-magnetic induction; electrical units; electromagnetic waves; electrolysis; the conduction of electricity through gases; radio-activity. The book is intended primarily for students of physics but can be read with profit by chemists. *Wilder D. Bancroft*

Physical Optics. *By Robert W. Wood. 15 × 23 cm; pp. vi + 546. New York: The Macmillan Company, 1905. Price: bound, $3.50.*—Professor Wood has done wisely in bringing together in a single volume the host of ingenious experiments which he has contrived, and adding adequate and systematic explanation. The book thus becomes not merely a treatise on optics but an exhibit of achievement, inasmuch as almost every one of the chapters is enriched by some striking accomplishment of the author's. Thus, to mention only a few, Chapters II. and III., on the propagation and reflection of light, contain his remarkable photographs of sound waves, his carefully constructed zone-plate, etc., and Chapter IV., on refraction, his mirage experiments. But it is in the

case of the later chapters, on dispersion, rotary polarization, magneto-optics, fluorescence, and scattering, that Professor Wood's most valuable work will be found. Apart from these personal contributions, however, the book is a systematic treatise full of information, and the author has spared no pains in adducing the theory of his subject, in each of the 22 chapters and in every essential case.

C. Barus

An Elementary Laboratory Course in Chemistry. *By Frank B. Kenrick and Ralph E. DeLury. 18 × 25 cm; pp. 90. Toronto: Morang and Co., 1905. Price: bound, $1.00.*—"The course of practical chemistry outlined in this book is intended for students who are beginning the subject and at the same time taking a course of lectures on general chemistry. It was arranged primarily for the first year arts course of the University of Toronto, in which all science students —whether they are taking chemistry for two years only or whether they intend to specialize in this subject—are required to do exactly the same work in their first year. It has been necessary therefore to keep in view the twofold object of giving the former class of students, in a very limited period, as fair an idea as possible of the general nature of chemistry, and at the same time, of providing the latter class with a good working basis for their subsequent course."

The different sections in the first part are: solution and crystallization; separation by solution; experiments with air; combustion of magnesium; properties of magnesium oxide; chemical substances, the composition of water; determination of weight of hydrogen given off when magnesium dissolves in an acid; the law of reacting weights; the properties and composition of acids; acids, bases and salts; solubility, separation by volatilization; properties of aqueous salt solutions; quantitative separation by solution; precipitation of copper oxide; proportion of copper in copper oxide; chemical reaction in solution, measurements of liquids; volumetric analysis; law of reacting weights in solution; volume relations of gases; some experiments to illustrate the influence of conditions on reactions; a reversible reaction; the mass law; applications of the mass law; dissociation of salts in water; some experiments on dissociation; application of mass law to dissociation; separation and identification of substances; solubility tables, principles of qualitative analysis, separation of "group I"; method of separating and identifying copper, bismuth, mercury (ic), cadmium, and lead (group II B).

The second part is devoted to qualitative analysis and there is an appendix in which the authors discuss: classification of substances; atomic weights and the periodic system; formula weights or molecular weights; valency; reversible reactions and equilibrium; rate of reaction; oxidation and reduction; further applications of the mass law and dissociation; extent of dissociation; experimental error; glass-blowing.

Whether this is a better way to teach elementary chemistry than the orthodox method is a matter to be settled by experiment. Certainly the method of the authors is quite different from that usually employed. It seems probable that a student who is taking chemistry as part of a liberal education would carry away more from a laboratory course like this than from the one he would get in most places. Whether it would be as good for the student intending to specialize in chemistry or medicine is more uncertain. Probably it would depend very largely on the nature of the lecture course accompanying the work.

In general, the experiments are well selected. The reviewer is not clear, however, how the student is to know that he has purified copper sulphate in the first experiment by recrystallizing it. It seems quite impossible for the student to answer the question as to what has become of any soluble impurities that may have been present. Experiments 7 and 8 are quite unintelligible outside of the Toronto laboratory because there is nothing to show what the mysterious "white substance" is with which the experiments are to be made. Barring these two points the authors are to be congratulated on their manual and we shall await with interest the results of the practical test of their innovation. Certainly no one will claim that our present methods of teaching elementary chemistry are the best possible. *Wilder D. Bancroft*

A Laboratory Guide to the Study of Qualitative Analysis; *based upon the Application of the Theory of Electrolytic Dissociation and the Law of Mass Action. By E. H. S. Bailey and Hamilton P. Cady. Fifth edition, thoroughly revised. 14 × 21 cm; pp. iv + 278. Philadelphia: P. Blakiston's Son and Co., 1905. Price: bound, $1.25.*—This book on qualitative analysis is based entirely on the dissociation theory. This in itself is good and the authors seem to have overcome the difficulties fairly successfully. It seems to the reviewer that in another edition, it might be well to use the dissociation theory in a less obtrusive manner. After showing that silver as ion is a test for chlorine as ion, it would be just as satisfactory to speak of chlorides as to speak of chlorine ions continually. The old statement that silver nitrate is a test for soluble chlorides is correct as soon as one gives a definition of what one means by chlorides. It seems to the reviewer that the words chlorides, nitrates, sulphates, etc., are good ones and that there is nothing to be gained by replacing them with such circumlocutions as compounds yielding chlorine as ion, etc. It would also be well to discuss the mass law and the solubility product from a more qualitative point of view. We know that addition of salt with a common ion usually decreases the solubility of the other salt. As we cannot tell when the rule is going to break down, the student should be taught to determine this point experimentally in each case.

It should be noticed that these suggestions refer merely to methods of phrasing and are not in any sense criticisms of the subject-matter or of the general treatment. Both of these are very satisfactory and there is no doubt that a student trained along these lines will have a clearer idea of what he is doing than will one who has received a more old-fashioned training. Fortunately, there are relatively few places now where qualitative analysis is taught without any reference being made to the electrolytic dissociation theory.

Wilder D. Bancroft

Le Matière, sa Naissance, sa Vie, sa Fin. *By P. de Heen. 16 × 24 cm; pp. 119. Brussels: Hayes, 1905.*—"Il ne peut y avoir pour le physician ni phlogistique, ni corpuscules, ni lumière, ni magnétisme, ni électricité. Il n'y a que gyrostats et tourbillons vibrants." The book is a development of the idea outlined in this quotation. The treatment is distinctly clever, and not especially convincing. The book should prove very interesting to those who care for speculations of this sort. *Wilder D. Bancroft*

Recherches sur le Temps que le Précipitation met a apparaitre dans les Solutions d'Hyposulfite. *By Gaston Gaillard. 17 × 25 cm; pp. 76. Paris: Gauthier-Villars, 1905.*—This is apparently the equivalent of a doctor thesis. The author has studied the effect of concentration, temperature, presence of acids, etc., on the rate of decomposition of the hyposulphites, attention being paid only to the time at which sulphur begins to precipitate. *Wilder D. Bancroft*

REVIEWS

The object of this department of the Journal is to issue, as promptly as possible, critical digests of all Journal articles that bear upon any phase of Physical Chemistry.

General

The atomic weight of chlorine. *H. B. Dixon and E. C. Edgar. Phil. Trans.* 205 *A*, *169* (*1905*).—Chlorine, made by the electrolysis of fused silver chloride, was condensed and weighed as a liquid in a sealed glass bulb. The hydrogen, prepared by the electrolysis of barium hydroxide, was dried and absorbed by palladium in a weighed vessel. The palladium on being warmed gave off the hydrogen, which was ignited by a spark and burned at a jet in the combustion globe previously filled with chlorine. The unburned chlorine, about two percent by volume, was determined by means of potassium iodide and thiosulphate in an atmosphere of carbonic acid. On the oxygen basis the value of chlorine becomes 35.463, practically identical with the 35.467 of Richards and Wells.

W. D. B.

The atomic weight of nitrogen. *R. W. Gray. Jour. Chem. Soc.*, 87, *1601* (*1905*).—From density determinations of nitric oxide the author deduces an atomic weight of 14.006 for nitrogen. Nitric oxide and pulverulent nickel were then heated together and the nitrogen absorbed in cocoanut charcoal. This gravimetric method leads to an atomic weight of 14.010 for nitrogen. The volumetric and gravimetric methods thus give nearly the same result, one which is quite different from the 14.04 of Stas.

W. D. B.

A revision of the atomic weight of cadmium. *G. P. Baxter and M. A. Hines. Zeit. anorg Chem.*, 44, *158* (*1905*).—Reviewed (9, 423) from *Jour. Am. Chem. Soc.*, 27, 22 (1905).

The design of gas regulators for thermostats. *T. M. Lowry. Jour. Chem. Soc.* 87, *1030* (*1905*).—The author recommends the use of toluene in a fluted or a spiral glass vessel. As was to be expected, these are much more efficient than the usual forms of regulator.

W. D. B.

One-Component Systems

The determination of melting-points at low temperatures. *L. F. Guttmann. Jour. Chem. Soc.*, 87, *1037* (*1905*).—A constantan-copper couple was used and the liquid to be studied was placed in a glass tube and dipped into a freezing-mixture contained in a Dewar vessel. The following melting-points were obtained:

Methyl alcohol,	— 97.8°	Ethyl chloride,	—141.6°
Ethyl alcohol,	—117.3	Ethyl bromide,	—117.8
m-Xylene,	— 54.8	Ethyl iodide,	—108.5
Ethyl benzene	— 92.8	Methyl iodide	— 64.4
Toluene	— 92.4		

W. D. B.

The latent heat of evaporation of benzene and some other compounds. *J. C. Brown. Jour. Chem. Soc.*, 87, 265 (1905).—When absolutely pure benzene is used a molecular heat of vaporization of 94.93 is obtained, which agrees with 94.4 obtained by Griffiths and Marshall, also with 93.5 found by Schiff. With benzene containing a little thiophene a value of 106.15 was obtained which agrees fairly with the value 107.6 obtained by Jahn for what he called pure benzene. Heats of evaporation were also determined for toluene (87.43), *o*-xylene (82.47), *m*-xylene (81.34), *p*-xylene (80.98), mesitylene (74.42), cymene (67.64).

W. D. B.

The physical properties of heptoic, hexahydrobenzoic, and benzoic acids, and their derivatives. *J. S. Lumsden. Jour. Chem. Soc.*, 87, 90 (1905).—The author has determined and tabulated a number of physical properties of heptoic, hexahydrobenzoic and benzoic acids, and also of the derivatives of these three acids.

W. D. B.

The use of quartz vessels in laboratories. *F. Mylius and A. Meusser. Zeit. anorg. Chem.*, 44, 221 (1905).—Alkali and hydrofluoric acid attack quartz at ordinary temperatures, and concentrated phosphoric acid reacts with it at 400°. Quartz absorbs methylene blue, Congo red or rhodamine from aqueous solution, aniline blue from alcoholic solution, and iodeosine from an ether solution. Water has no appreciable action on quartz at 100° and neither does concentrated sulphuric acid at the same temperature.

W. D. B.

Two-Component Systems

Silver-aluminum alloys. *G. I. Petrenko. Zeit. anorg. Chem.*, 46, 49 (1905).—The author has determined the freezing-point curve for this series and decides that there are two compounds, neither of which is stable at its melting-point. Aluminum forms solid solutions with silver to the extent of 4 percent according to the pyrometric evidence, but the microscopic section shows the presence of two phases at 3 percent Al. The discrepancy did not appeal to the author. The most stable of these compounds is $AlAg_2$. Between 25 and 35 atomic percents of aluminum, the freezing-point curve is thought to indicate the existence of homogeneous solid solution of $\beta AlAg_2$ and $\beta AlAg_3$. Owing to an error in the way of lettering the diagram, the region for this homogeneous solid solution is marked so that one might infer that two kinds of crystals were present, thus making five phases necessary over a range of concentrations and temperatures. This is presumably not the author's conception; however, the discussion of these forms is too scanty to make certain. In fact, the grounds for believing in the existence of the β-form of $AlAg_2$ are quite insufficient. The compound $AlAg_3$ is not stable in contact with the melt, but forms from a decomposition of a solid solution. The eutectic for aluminum and $AlAg_2$ occurs at 565° and 30 per cent of aluminum. By using atomic percents a part of the time and weight percents at other times, the author makes the paper quite confusing. There is no statement to the effect that, by any method of annealing and quenching, the author has shown that those regions which should be homogeneous are so. It is thought that silver does not form solid solutions with aluminum. The conclusions throughout are based upon the pyrometric evidence, and must therefore be regarded as insufficient.

E. S. S.

Gold-tin alloys. *R. Vogel. Zeit. anorg. Chem.*, 46, 60 (1905).—From the freezing-point curve the author deduces the existence of a solid solution of tin in gold to about 4 percent and the compounds AuSn, $AuSn_2$, $AuSn_4$. It seems a little odd to quote Maey's determinations and supplement them with the old figures of Holzmann as giving the specific volume of these alloys. It would have seemed to be no extraordinary amount of labor had the author determined the density of the alloys which he studied. This is especially true since the author carefully points out that unless the alloys are properly made, they do not reach equilibrium, and it seems probable therefore that both Maey and Holzmann determined the density of alloys which were not in equilibrium and whose densities do not bear any relation to the freezing-point curve as determined by the author. The same criticism applies to his quoting the electrical conductivity and the electromotive force as determined many years ago.

E. S. S.

Alloys of magnesium with tin and thallium. *G. Grube. Zeit. anorg. Chem.*, 46, 76 (1905).—In the case of magnesium and tin, the author believes he has shown the existence of a compound $SnMg_2$. This compound melts at 783°. The eutectic between this compound and magnesium is at 560° and 41 percent of magnesium. The eutectic in which tin is the second phase is at 210° and about 3 percent of magnesium. The curve for magnesium and thallium shows evidence for the existence of a solid solution of thallium in magnesium to about 8 percent, and of three compounds, Tl_2Mg_8, $TlMg_2$, Tl_2Mg_5. While the evidence is not conclusive, the above results will have to be admitted, pending a repetition of the work in a more systematic manner. *E. S. S.*

Alloys of sodium and tin. *C. H. Mathewson. Zeit. anorg. Chem.*, 46, 94 (1905).—From pyrometric data, the author is led to believe in the existence of Na_4Sn, Na_4Sn, Na_4Sn_2, NaSn and $NaSn_2$. The alloys are unquestionably difficult to study, and this is the first attempt at a systematic investigation. Some of the results obtained cannot be explained in the way suggested by the author, and one would feel more confidence in all of them if such implicit faith were not placed on pyrometric data. *E. S. S.*

Alloys of iron and silicon. *W. Guertler and G. Tammann. Zeit. anorg. Chem.*, 47, 163 (1905).—The authors have determined the freezing-point curve for these alloys. They find a pronounced maximum at the composition FeSi, and evidence for believing in the existence of Fe_2Si. Fe_4Si is said to form a homogeneous solid solution with iron, but eutectic combinations with FeSi. FeSi and Si form a eutectic series. The effect of silicon on the heat changes accompanying the allotropic modifications of iron was not investigated. *E. S. S.*

Alloys of aluminum and antimony. *G. Tammann. Zeit. anorg. Chem.*, 48 53 (1905).—The author has not studied these alloys, but proposes an explanation for the abnormal curves obtained by Gautier and by Campbell and Mathews. It is suggested by the author that the compound AlSb forms with considerable slowness, and that for that reason the alloys investigated by the previous students were not in equilibrium. By a very pretty experiment, this is shown to be the case, but owing to lack of time and the difficulties involved in a systematic study of the series, the constitution is not further investigated. While

the explanation suggested by the author accounts beautifully for one of the maxima, it leaves one somewhat in doubt as to the reason for the existence of the other. The case is of interest since it points out very clearly the fact that the time factor must be considered in any systematic investigation of alloys. This is especially interesting in view of the many alloy papers emanating from the author's laboratory in which papers the time factor is in no way considered.

E. S. S.

Researches on the freezing-points of binary mixtures of organic substances. *J. C. Philip and S. H. Smith. Jour. Chem. Soc.*, 87, *1735* (*1905*).—The authors have determined complete freezing-point curves for mixtures of catechol, resorcinol or quinol with picric acid, *p*-toluidine or *a*-naphthylamine; also for mixtures of guaiacol and picric acid. Owing to decomposition, accurate results could not be obtained for quinol and picric acid. In each of the other nine systems at least one compound was shown, most of the compounds being stable at their melting-points. *W. D. B.*

Solubility of zinc chloride. *F. Mylius and R. Dietz. Zeit. anorg. Chem.*, 44, *209* (*1905*).—The complete solubility diagram for zinc chloride and water has been determined. On the zinc chloride side the solid phases are anhydrous zinc chloride and hydrates with 1, 1.5, 2.5, 3 and 4 of water. Although anhydrous zinc chloride ceases to be the stable form at 28°, its solubility curve can be followed down to 10°. The hydrates with 2.5 and with 3 of water are stable at their melting-points. *W. D. B.*

The solubility of potassium chloride, bromide, and iodide in water. *A. Meusser. Zeit. anorg. Chem.*, 44, *79* (*1905*).—The author has determined boundary curves for water with potassium chloride, bromide and iodide at temperatures beween 0° and the eutectic temperatures. *W. D. B.*

Studies in comparative cryoscopy. III. *P. W. Robertson. Jour. Chem. Soc.*, 87, *1574* (*1905*).—Freezing-point determinations were made for esters in phenol as solvent. Many of the monobasic esters show a decreasing apparent molecular weight with increasing concentration. *W. D. B.*

Solubility as a measure of the change undergone by isodynamic hydrazones. *W. Robertson. Jour. Chem. Soc.*, 87, *1298* (*1905*).—Camphorquinone phenylhydrazone changes to another modification when dissolved in benzene; but this change takes place so slowly that it is possible to determine the solubility of the unchanged modification as well as the final solubility. *W. D. B.*

The basic properties of oxygen at low temperatures. *D. McIntosh. Jour. Chem. Soc*, 87, *784* (*1904*).—At low temperatures methyl and ethyl alcohol form addition products with one of chlorine or one of bromine. The ethers form similar addition products but with two of chlorine or of bromine. *W. D. B.*

The determination of molecular weight by lowering of vapor pressure. *E. P. Perman. Jour. Chem. Soc.*, 87, *194* (*1905*).—The author describes an apparatus for measuring the lowering of the vapor-pressure of a solution at constant temperature. This is distinctly a step in the right direction and it is to be hoped that the author will use his apparatus as an instrument of research, studying the behavior of concentrated solutions. *W. D. B.*

Application of the microscopic method of molecular weight determinations to solvents of high boiling-point. *G. Barger and A. J. Ewins. Jour. Chem. Soc.*, 87, 1756 (1905).—The authors have devised a hot stage for a microscope so that determinations of molecular weights by the microscopic method (9, 427) can be made at higher temperatures. *W. D. B.*

New method of determining molecular weights. *P. Blackman. Jour. Chem. Soc.*, 87, 1474 (1905).—Two solutions are isotonic when the vapor-pressures are equal. A solution of one non-volatile solute is placed in one graduated tube and a solution of another non-volatile solute in the same solvent is placed in another graduated tube. The two tubes are connected with each other and with the outside air. The solutions in the tubes are then boiled until equilibrium is reached and the relative volumes measured. The method is ingenious but not very accurate. *W. D. B.*

Multi-Component Systems

Influence of various sodium salts on the solubility of sparingly soluble acids. *J. C. Philip. Jour. Chem. Soc.*, 87, 987 (1905).—The author has determined the solubility of cinnamic, benzoic and *o*-nitrobenzoic acids in solutions containing sodium butyrate, acetate, formate or salicylate; also the solubility of salicylic acid in solutions of the first three salts. The qualitative results are what the theory requires. Although the author gives a cut showing the theoretical quantitative results, he does not do more than to call attention to the general similarity between that cut and the one for the experimental data. *W. D. B.*

The influence of water and alcohols on the boiling-point of esters. I. *J. Wade. Jour. Chem. Soc.*, 87, 1656 (1905).—Ethyl acetate and water form two liquid layers with a boiling-point below that of either of the components. Ethyl acetate and alcohol have a minimum boiling-point and there is a ternary mixture of ethyl acetate, alcohol and water which boils lower than either of the binary mixtures. The author discusses the bearing of these phenomena on the preparation of ethyl acetate. *W. D. B.*

The molecular condition in solution of ferrous oxalate. *S. E. Sheppard and C. E. K. Mies. Jour. Chem. Soc.*, 87, 189 (1905).—In ferrous oxalate solutions the iron is present chiefly as the complex anion $Fe(C_2O_4)_2''$. Spectrophotometric measurements showed that the dissociation

$$Fe(C_2O_4)_2'' \rightleftharpoons Fe'' + 2C_2O_4''$$

is negligible at moderate concentrations. In presence of solid FeC_2O_4 the ratio of the concentrations of $Fe(C_2O_4)_2''$ and C_2O_4'' is constant. *W. D. B.*

Polysulphides. II. *F. W. Küster. Zeit. anorg. Chem.*, 44, 431 (1905).—The dissolving of sulphur in sodium sulphide solution can be followed up to the saturation point by means of potential measurements. The Nernst formula describes the facts for platinum or silver electrodes in solutions containing sulphur and sodium polysulphides. The sulphur up to Na_2S_4 is held more firmly than any in excess of these proportions. *W. D. B.*

Bromine in solutions of potassium bromide. *F. P. Worley. Jour. Chem. Soc.*, 87, 1107 (1905).—The additional solubility of bromine in dilute solutions

of potassium bromide is apparently due to the quantitative formation of KBr_3. For higher concentrations of potassium bromide, it is necessary to assume the formation of other compounds. *W. D. B.*

The action of carbon monoxide on ammonia. *H. Jackson and D. Northall-Laurie. Jour. Chem. Soc.*, 87, 433 (1905).—"When a mixture of dry carbon monoxide and ammonia is heated in the presence of platinum, subjected to the silent electrical discharge, to electric sparking, or treated with the high frequency current, combination occurs, and ammonium cyanate is formed as the main product, which, as the temperature rises, is rapidly converted into carbonate."

The main reaction appears to be

$$CO + 2NH_3 = NH_4CNO + H_2.$$

Small amounts of cyanide are also formed, presumably according to the equation

$$CO + 2NH_3 = NH_4CN + H_2O.$$

In the gaseous phase are to be found small and varying amounts of methane and nitrogen while some condensation products of the cyanide are found in the bottom of the flask as brown solids. *W. D. B.*

Association in mixed solvents. *G. Barger. Jour. Chem. Soc.*, 87, 1042 (1905).—The author has determined the apparent molecular weights of various substances in mixed solvents by his method (9, 427). Since we have no way of calculating molecular weights in mixed solvents, the author's results have not the significance which he attaches to them. *W. D. B.*

The iodides of copper. *J. W. Walker and M. V. Dover. Jour. Chem. Soc.*, 87, 1584 (1905).—A study of the behavior of cuprous iodide and iodine solution. Use is made of the mass law rather than of the phase rule and the authors are therefore never certain whether they are analyzing mixtures or not. *W. D. B.*

The formation of magnesia from magnesium carbonate by heat, and the effect of the temperature on the properties of the product. *W. C. Anderson. Jour. Chem. Soc.*, 87, 257 (1905).—Commercial carbonate of magnesia is sold by Merck in three brands "heavy," "light" and "crystal." The author writes the following formulas $20MgCO_3.21MgO_2H_2.62H_2O$, $14MgCO_3.10MgO_2H_2.75H_2O$, and $19MgCO_3.20MgO_2H_2.65H_2O$ respectively. He therefore deduces very high molecular weights for these alleged compounds. As no effort was made to prove that these substances were homogeneous, the analyses and the conclusions really mean nothing. On heating these samples in a current of air, the 'heavy' carbonate began to lose CO_2 at 368°, the 'light' carbonate at 352°, and the 'crystal' carbonate at 271.5°. Tests were then made on the rates of solution of magnesia made by heating these different carbonates to different temperatures. No thorough stirring was used and no attempt was made to determine the surface. The general result is that the rate of solution depends on the previous history of the magnesia. The work was carried out under a grant from the Scottish Carnegie Research Fund and cannot therefore have been done twenty years ago. *W. D. B.*

The reduction of metallic oxides by aluminum carbide. *J. N. Pring. Jour. Chem. Soc.*, 87, 1530 (1905).—Aluminum carbide was prepared by heating

aluminum in an arc furnace. The reaction is apparently between the aluminum and the carbon monoxide from the limestone blocks and the electrodes. Aluminum carbide reacts slowly with copper oxide at a dull red heat, readily in presence of fused cryolite as flux. At 1500° aluminum carbide reacts energetically with molten copper. *W. D. B.*

Solid solutions. *R. F. Korte. Jour. Chem. Soc.*, 87, 1503 (1905).—The author cites experiments to prove that the carrying down of iron by barium sulphate is not a case of solid solution. The carrying down of magnesium oxalate by calcium oxalate, of manganese hydroxide or nickel hydroxide by ferric hydroxide are believed to be due to the formation of a solid solution. The apparent carrying down of nickel or manganese hydroxide by aluminum hydroxide appears to be solely a case of mechanical inclusion. *W. D. B.*

The rusting of iron. *W. R. Dunstan, H. A. D. Jowett and E. Goulding. Jour. Chem. Soc.*, 87, 1548 (1905).—"In the ordinary atmospheric rusting of pure iron electrolytic action does not occur and no hydrogen is set free in the process.

"We consider that the results of this investigation prove conclusively that iron, oxygen, and liquid water are alone necessary for the rusting of iron to take place. Under atmospheric conditions, carbon dioxide plays a quite subordinate part in the process. One of the simplest representations to the chemical action between iron, oxygen and liquid water presupposes the intermediate formation of hydrogen peroxide. Although the actual production of this substance has not been demonstrated, a considerable body of experimental evidence has been obtained in favor of its temporary formation. We have also shown that the conditions of the spontaneous oxidation of iron known as rusting presents peculiarities which are not shared by other processes in which iron undergoes oxidation with formation of a ferric hydroxide. *W. D. B.*

Solution and pseudo-solution. *E. Linder and H. Picton. Jour. Chem. Soc.*, 87, 1906 (1905).—"We have shown that the physical and chemical properties of arsenious sulphide and ferric hydroxide are closely analogous. Both are representative of important groups of colloids—arsenious sulphide of the 'acidic,' electro-negative group, ferric hydroxide of the 'basic,' electro-positive group. Both are capable of existing in every grade of pseudo-solution. Of these grades, the highest exhibit properties which place them on the very border line between emulsions and true solutions. Of the two, ferric hydroxide possesses these properties in the most marked degree: it is filterable through a porous cell, dialyses (with extreme slowness), diffuses, re-dissolves on freezing, is not coagulated by boiling; either alone or with precipitated barium sulphate, expands sensibly on coagulation, and gives rise by direct ionic exchange to a series of stable derivatives. It has one property only which distinguishes it in marked degree from 'true' solutions, such as aqueous solutions of soluble blue or methyl-violet, it scatters and polarises light, proving that it contains particles of dimensions commensurable with the wave-length of light. The study of these high-grade colloids, therefore, opens up questions of the highest interest; the phenomena of their solution and de-solution afford an insight into the laws which govern the solubility of substances in water under conditions not complicated by dissociation phenomena." *W. D. B.*

Inorganic colloids. *A. Gutbier and G. Hofmeier. Zeit. anorg. Chem.*, 44, *224* (*1905*).—It was not found possible to obtain a bismuth hydrosol by reduction with hydrazine. Hypophosphorous acid proved effective. With hydrazine as reducing agent in a solution containing gum-arabic, it was possible to prepare hydrosols of copper and of mercury. *W. D. B.*

Silicic acid. III. *E. Jordis. Zeit. anorg. Chem.*, 44, *200* (*1905*).—The author reiterates the statement that a pure silicic acid hydrosol is theoretically impossible and describes his method of making a pure gel. *W. D. B.*

The thermal decomposition of formaldehyde and acetaldehyde. *W. A. Bone and H. L. Smith. Jour. Chem. Soc.*, 87, *910* (*1905*).—At high temperatures formaldehyde breaks down chiefly into carbon monoxide and hydrogen. Traces of methane are found. When the vapor of formaldehyde is kept under considerable pressure at 350° in borosilicate glass bulbs, some condensations or polymerizations take place. At 400° acetaldehyde breaks down nearly completely into methane and carbon monoxide. At 600° some carbon and hydrogen are also found. When the undiluted vapor of acetaldehyde is passed slowly over a surface of porous porcelain heated to 450°–500°, a condensable liquid is formed consisting chiefly of unsaturated aldehydes; carbon is precipitated; and the gas contains ethane. *W. D. B.*

The synthesis of formaldehyde. *D. L. Chapman and A. Holt, Jr. Jour. Chem. Soc.*, 87, *916* (*1905*).—When hydrogen is heated with carbon dioxide, and when carbon monoxide (alone or mixed with hydrogen) is heated with steam by means of platinum wire, formaldehyde is produced in considerable quantity. The essential condition is that there shall be liquid water present to take up the formaldehyde as fast as formed. *W. D. B.*

The combustion of acetylene. *W. A. Bone and G. W. Andrews. Jour. Chem. Soc.*, 87, *1232* (*1905*).—In a sealed tube acetylene and oxygen begin to react at 250°. The temperature is lowered by increasing the pressure. An excess of oxygen decreases the rate of reaction while an excess of acetylene has little effect. There is *no* preferential oxidation of carbon or oxygen; carbon monoxide and formaldehyde arise simultaneously during the slow combustion of acetylene and are probably formed from the instable compound COH : COH. There was no formation of benzene. In contact with a hot catalyzing surface, such as porous porcelain, acetylene unites with steam, forming acetaldehyde. *W. D. B.*

Estimation of potassium permanganate in the presence of potassium persulphate. *J. A. N. Friend. Jour. Chem. Soc.*, 87, *438* (*1905*).—Potassium permanganate in dilute aqueous solution can be determined iodometrically in presence of potassium persulphate provided only a slight excess of acid is added and that but little sulphuric acid is present. *W. D. B.*

Osmotic Pressure and Diffusion

Behavior of solutions of propyl alcohol toward semipermeable membranes. *A. Findlay and F. C. Short. Jour. Chem. Soc.*, 87, *819* (*1905*).—Pickering has stated that water or propyl alcohol will pass through a porous cup but that a mixture of the two does not. The experiments of the authors force them "to

conclude that the anomalous behavior of solutions of propyl alcohol in water described by Pickering, unless confirmed by other experiments, is to be accounted for most probably (if the possibility of experimental error is excluded) by differences in the velocity of diffusion. If this be so, the rise of liquid in the pot could only have been temporary, and the experiment would hence lose all its significance for the problem of solution." *W. D. B.*

Velocities

The chemical dynamics of the reactions between sodium thiosulphate and organic halogen compounds. *A. Slator. Jour. Chem. Soc.*, 87, 481 (1905).—The author has studied the reaction between thiosulphate and halogen-substituted acetates

$$CH_2BrCO_2C_2H_5 + Na_2S_2O_3 = NaS_2O_3.CH_2CO_2C_2H_5 + NaBr.$$

The reaction is bimolecular. Addition of silver nitrate decreases the activity of the thiosulphate in such a way as to render a portion of the thiosulphate inactive corresponding with the formation of the compound $Na_3Ag(S_2O_3)_2$. Lead nitrate has a similar effect. *W. D. B.*

The kinetics of chemical changes which are reversible. *C. E. Fawsitt. Jour. Chem. Soc.*, 87, 494 (1905).—The author has studied the effect of hydrochloric acid on the unsymmetrical dimethylcarbamide

$$CO(NH_2).N(CH_3)_2 + 2HCl + H_2O = NH_2(CH_3)_2Cl + NH_4Cl + CO_2.$$

"The decomposition of the substances of the carbamide group by acids is due to a transformation into cyanate, which is then decomposed by the acid. The transformation into cyanate is proportional to the concentration of the amide.

"Whilst a small increase of the acid concentration, starting from a dilute solution, does not affect the velocity of decomposition of these amides, the effect of a large increase of concentration is to retard the velocity. This retardation is due to the removal of some amide from the active amount of decomposing substance owing to salt formation.

"*as*-Dimethylcarbamide decomposes with acid at about six to seven times the rate at which carbamide decomposes. The velocity of decomposition of *as*-dimethylcarbamide with alkalies is of the same order as that with acids." *W. D. B.*

Esterification constants of substituted acrylic acids. I. *J. J. Sudborough and D. J. Roberts. Jour. Chem. Soc.*, 87, 1845 (1905).—The authors have determined and tabulated the esterification constants for twenty-three acids in methyl alcohol solution with hydrochloric acid as catalytic agent. *W. D. B.*

The influence of the hydroxyl and alkoxyl groups on the velocity of saponification. I. *A. Findlay and W. E. S. Turner. Jour. Chem. Soc.*, 87, 747 (1905).—Experiments on the rate of saponification of the esters of mandelic acid and the substituted mandelic acids. Introduction of a hydroxyl group increases the rate of saponification while replacing the hydrogen of the hydroxyl group by an alkyl radical diminishes it. *W. D. B.*

On hydrofluoric acid. *E. Deussen. Zeit. anorg. Chem.*, 44, 300, 408 (1905).—Inversion experiments show that hydrofluoric acid is not a strong acid. In

n/4 solutions it is about equal to monochloracetic acid; in more dilute solutions it is relatively weaker. The behavior of hydrofluoric acid on dilution lies between that of a monobasic and of a dibasic acid. Commercial hydrofluoric acid dissolves iron rust much more rapidly than does an equivalent solution of hydrochloric acid. *W. D. B.*

The arsenic anhydride catalysis of sulphur trioxide. *E. Berl. Zeit. anorg. Chem.*, 44, 267 (1905).—Arsenic anhydride is about as efficient a catalytic agent as ferric oxide in the manufacture of sulphur trioxide. If the gases are dried over phosphorus pentoxide, the reaction velocity is decreased. The best amount of water vapor is that which is in equilibrium with concentrated sulphuric acid. In the process we are dealing with the combined effects of diffusion and of chemical reaction. Sulphur trioxide checks the rate by not diffusing away from the surface of the catalytic agent. *W. D. B.*

The formation of ammonia from the elements. *F. Haber and G. van Oordt. Zeit. anorg. Chem.*, 44, 341 (1905).—At 1020° C and under one atmosphere pressure the equilibrium between ammonia, nitrogen and hydrogen corresponds to 0.012 percent ammonia. At a red heat we have the two reactions taking place

$$Ca_3N_2 + 3H_2 \rightleftharpoons 3CaH_2 + N_2.$$

and

$$N_2 + 3H_2 \rightleftharpoons 2NH_3.$$

The catalytic action disappears to all intents and purposes before the temperature has fallen to a point at which the equilibrium concentration of ammonia really amounts to anything. The temperature relations with manganese nitride are a little better than with calcium nitride; but in neither case is there any probability of the method being feasible on a large scale. *W. D. B.*

Electromotive Forces

Oxidation equilibria and differences of electro-affinity. *J. F. Spencer and R. Abegg. Zeit. anorg. Chem.*, 44, 379 (1905).—The tendency of thallic salts to change into thallous salts is given by the equation

$$Tl''' \rightarrow Tl' = 1.199 + 0.029 \log \frac{Tl'''}{Tl'}.$$

As required by this formula, dilution of a mixture of thallic and thallous salts has no effect on the potential difference. Owing to the tendency of thallium cations to form complex salts with various anions, the thallic-thallous potential may vary from 1.199 to 0.126 volt. Equilibrium between platinum and oxygen or a thallium salt is reached more quickly when the other is also present in the solution. Under these circumstances a value of 1.1385 ± 0.001 volt is obtained for the oxygen potential. *W. D. B.*

Anodic decomposition phenomena with salts of thallium, bismuth and silver. *M. Bose. Zeit. anorg. Chem.*, 44, 237 (1905).—There is a decomposition point for thallium nitrate at 1.428 volts corresponding to the oxide Tl_2O_3, and a suggestion of one at 1.08 volts but it is not known to what oxide this refers. In bismuth nitrate solution there is a point at 1.86 volts, corresponding apparently

to the yellow oxide, Bi_2O_3. At higher voltages there is an evolution of oxygen containing a relatively large amount of ozone. With silver nitrate there is a point at 1.573 volts corresponding probably to the oxide Ag_2O_3. *W. D. B.*

Electrolysis and Electrolytic Dissociation

Electrolytic oxidation of aliphatic aldehydes. *H. D. Law. Jour. Chem. Soc., 87, 198 (1905).*—During the electrolytic oxidation of an aldehyde, the decomposition products are the acid, carbon dioxide, carbon monoxide and a hydrocarbon. The formation of carbon monoxide is not explained. The author believes that the reaction takes place as follows:

$$RCHO + O = ROH + CO.$$

He was not able, however, to show the presence of alcohol in the solution.
W. D. B.

Studies in chlorination. II. *J. B. Cohen, H. M. Dawson and P. F. Crosland. Jour. Chem. Soc., 87, 1034 (1905).*—Current from carbon electrodes was passed through a boiling solution of toluene and concentrated hydrochloric acid. The rate of chlorination appears to be more rapid than with chemically-prepared chlorine. The chlorine enters the benzene ring. *W. D. B.*

Studies in chlorination. III. *J. B. Cohen and P. Hartley. Jour. Chem. Soc., 87, 1360 (1905).*—The authors have studied the products obtained by the progressive chlorination of benzene in presence of the aluminum-mercury couple. The remarkable feature about the work was that, except in the case of monochlorbenzene, each step in the chlorination gave rise to but one product.
W. D. B.

The electrical conductivities of some salt solutions in acetamide. *J. W. Walker and F. M. G. Johnson. Jour. Chem. Soc., 87, 1597 (1905).*—By repeated crystallization the authors obtained acetamide which had a specific conductivity of only 4.3×10^{-5} at 100°, about one-sixth the value obtained by Walden. Potassium iodide, chloride and cyanide in acetamide solution have about the same molecular conductivity. With potassium iodide a maximum molecular conductivity is obtained at a dilution of 30-40 liters. With mercuric chloride the molecular conductivity decreases with increasing concentration. *W. D. B.*

The halogen hydrides as conducting solvents. *B. D. Steele, D. McIntosh, and E. H. Archibald. Phil. Trans., 205A, 99 (1905).*—The authors give measurements of the vapor-pressures, densities, surface energies, and viscosities of the liquefied hydrides of chlorine, bromine, iodine, sulphur, and phosphorus.

"The solvent action of these substances has also been investigated, and we have shown that, with the exception of phosphuretted hydrogen, they are all able to act as ionising solvents, and the conductivity, molecular weight, and transport number of certain dissolved substances have been measured.

"The results of the measurements, although abnormal, are not inconsistent with the ionic theory; since we have shown that:—

"(1) If in a given solution the electrolyte is a compound containing n molecules of the dissolved substance, the concentration of this compound will be proportional to the nth power of the concentration of the dissolved substance, and therefore the expression for the molecular conductivity of the *electrolyte* be-

comes KV^n instead of KV. We have also shown that $KV^n = \alpha K'$, and that therefore the molecular conductivity of the *electrolyte* increases with dilution in these solutions in the same manner as in aqueous solutions. The variation of the molecular conductivity of the electrolyte with dilution is probably complicated by the occurrence of compounds which contain a different number of solvent molecules at different dilutions.

"(2) The want of agreement between conductivity and cryoscopic measurements is a necessary consequence of the occurrence of polymers or compounds in solution, and may be taken as evidence of the existence of such compounds.

"(3) The conduction of organic substances when dissolved in the halogen hydrides is best explained by the occurrence of electrolytic compounds of the organic substance with solvent. Transport number measurements have shown that the organic substance is carried to the cathode as a component of the complex cation." *W. D. B.*

The purification of water by continuous fractional distillation. *W. R. Bousfield. Jour. Chem. Soc.*, 87, 740 (1905).—Steam is led into a chamber in which there are two tubes filled with water at about 80° and two tubes filled with water kept at about 20°. A water with low conductivity condenses on these latter tubes while a poorer quality of water condenses on the hot tubes. It is claimed that water can thus be obtained having a conductivity not much above one reciprocal megohm per centimeter cube. No explanation is offered. *W. D. B.*

Pyridine as solvent and dissociating medium for inorganic salts. *J. Schroeder. Zeit. anorg. Chem.*, 44, 1 (1905).—The author finds that many reactions take place very rapidly in pyridine solution. He concludes that substances are electrolytically dissociated in pyridine solution. He hopes to be able to prove the existence of this dissociation in some satisfactory manner. *W. D. B.*

Dielectricity and Optics

The dielectric constants of phenols and their ethers dissolved in benzene and xylene. *J. C. Philip and D. Haynes. Jour. Chem. Soc.*, 87, 998 (1905).—The dielectric constant does not follow an additive law for solutions of phenol, anisol, *o*-tolyl methyl ether, *p*-tolyl methyl ether in benzene, nor for phenol or anisol in *m*-xylene. *W. D. B.*

Syntheses by means of the silent electric discharge. *J. N. Collie. Jour. Chem. Soc.*, 87, 1540 (1905).—When the silent discharge is passed through a mixture of ethylene and carbon monoxide cooled below zero, condensation takes place and a resinous hydrocarbon is formed. Traces of acroleine were also obtained. *W. D. B.*

Molecular refractions of some liquid mixtures with constant boiling-point. *I. F. Homfray. Jour. Chem. Soc.*, 87, 1430 (1905).—There is nothing about the molecular refraction of constant boiling mixtures of liquids to warrant the assumption of a compound. Other tests also gave negative results. *W. D. B.*

Molecular refractions of dimethylpyrone and its allies, and the quadrivalency of oxygen. *I. F. Homfray. Jour. Chem. Soc.*, 87, 1443 (1905).—It is shown

that the molecular refractions of a number of compounds can be calculated with a satisfactory degree of accuracy provided we assign a value of 2.73 to quadrivalent oxygen. *W. D. B.*

The influence of solvents on the rotation of optically active compounds. VII. *T. S. Patterson and F. Taylor. Jour. Chem. Soc.*, 87, 122 (1905).—This paper contains experiments on the solution-volume and rotation of menthol and menthyl tartrates.

"We consider that, on the whole, these results help to confirm the suggestion that rotation in solution and molecular-solution-volume are closely related phenomena. For menthol, the facts are in complete agreement with theory. With menthyl tartrate, the results for alcohol and nitrobenzene are in agreement, although the relationship between the two variables in benzene is anomalous. Difficulties are met with for menthyl diacetyl tartrate also, but here, as has been pointed out, although in alcohol and benzene the relationship is not a quantitative one, it is in agreement with theory, in so far as, in both cases, contraction brings about increased rotation. Thus out of the nine examples studied, contraction produces increased rotation in four instances, expansion causes diminished rotation in one case, while expansion accompanies increased rotation in another. Thus, out of nine observations, seven are in accord with the theory, and of the two exceptions one at least is somewhat doubtful."

W. D. B.

The influence of solvents on the rotation of optically active compounds. VIII. *T. S. Patterson. Jour. Chem. Soc.*, 87, 313 (1905).—Chloroform lowers the optical rotation of ethyl tartrate even causing a change of sign. The effect is more marked the greater the amount of chloroform and the lower the temperature. Dilution with chloroform gradually increases the solution-volume of the ester, which is in line with the author's theory. *W. D. B.*

The absorption spectra of uric acid, murexide and the ureides in relation to color and to their chemical structure. *W. N. Hartley. Jour. Chem. Soc.*, 87, 1796 (1905).—

1. Simple ureides exhibit spectra without absorption bands.

2. The linking together of two simple ureides by one or more polyvalent atoms causes a powerful selective absorption, which is destroyed when the rings are disunited by hydrolysis or otherwise.

3. The purin compounds cause the production of bands in their spectra when a C:O group is converted into an ethylenic linking within the ring and a C-OH group adjoining it.

4. The purin compounds show spectra with selective absorption, which increases in intensity with the number of C:O groups in the ring; it is strongest with trioxypurins, less well defined in dioxypurins, and feeble or altogether absent from monoxypurins.

5. The formation of alkaline salts intensifies absorption bands or produces color, and indefinite bands become well defined in presence of an alkali.

6. The complete and instantaneous conversion of dialuric acid into alloxantin has been measured with quantitative precision on photographed spectra of its solution, and the alloxantin has been shown to undergo further change as a result of hydrolysis.

7. The essential conditions for the formation of a color such as murexide are, first, the linking of two oximinoketone rings by oxygen or by nitrogen; second, the formation of one or more ethylenic linkings within the rings; and, third, the formation of a salt from the compound. *W. D. B.*

Observations on chemical structure and those physical properties on which the theory of color is based. *W. N. Hartley. Jour. Chem Soc.*, 87, *1822* (*1905*).—It is shown "that Kekulé's view of the constitution of benzene affords an explanation of the absorption bands in its spectrum.' The condensation of the carbon atoms (usually designated double and treble linking) at different points in the molecule must give rise to greater refractive and dispersive powers at those points, as we know, from the researches of Gladstone and of Brühl, they do in the whole molecule, and just as they also increase the actinic absorption. If these condensations and expansions (alternate double and single linkings) in the molecule of benzene are continually in progress, it may be possible to explain how color may result therefrom when light agitates the molecule."

W. D. B.

The ultra-violet absorption spectra of certain diazo-compounds in relation to their constitution. *J. J. Dobbie and C. K. Tinkler. Jour. Chem. Soc.*, 87, *273* (*1905*).—The *syn* and *anti* forms of potassium diazosulphonate give identical ultra-violet absorption spectra. The spectra are nearly, though not quite identical for the two diazocyanides obtained from *p*-anisidine and for the two from *p*-chloraniline. On the other hand, the diazonium cyanide from *p*-anisidine has a characteristic spectrum. The two isomeric potassium benzene diazotates have very different spectra. The same is true for the two compounds obtained by the action of caustic alkali on diazotized sulphanilic acid. *W. D. B.*

The ultra-violet absorption spectra of certain enol-keto-tautomerides. I. *E. C. C. Baly and C. H. Desch. Jour. Chem. Soc.*, 87, *766* (*1905*).—For solutions varying in concentration from *n*/100 to *n*/10,000 the authors draw the following conclusions:

1. In the case of the aliphatic tautomeric substances, neither the pure ketonic nor the pure enolic form gives an absorption band.

2. In solutions of the strength dealt with by us the pure ketonic form is almost diactinic, while the pure enolic form exerts a small general absorption.

3. When an absorption band is given, it means that the ketonic and enolic forms are coexistent and in dynamic equilibrium with one another—that is to say, a number of the molecules are oscillating between the two conditions.

4. The persistence of the absorption band, that is to say, the relative change of dilution or of thickness of the solution during which the absorption band can be observed, is a measure of the number of molecules in the changing state.

4*a*. In order that the absorption band may be developed it is probably necessary that a considerable number of the molecules must be in the changing state.

5. The addition of alkali tends to increase the persistence of the band, while the addition of acid tends to decrease it.

6. The successive addition of alkali increases the persistence of the band, until a maximum is reached, beyond which the further addition of alkali does not increase it.

7. The absorption bands are given by the aluminum derivatives of the tautomeric substances as well as by their sodium derivatives, the former compounds are soluble in alcohol, and are neither hydrolyzed nor ionized.

8. The oscillation-frequency of the absorption band bears no relation to the mass of the atom in the labile state.

9. The absorption band is due to the change of linking accompanying the change from one form to the other, and its formation may be explained by the modern physical conception of the atom as a system of electrons.

10. The labile atom may be regarded as a potential ion, inasmuch as the bond of attraction or Faraday tube of force must be considered to be lengthened sufficiently to allow of the interchange of the atom from one position to the other within the molecule; the action of alkali and acid may thus be considered to have the effect of lengthening or shortening these tubes of force, thereby increasing or decreasing the number of interchanges taking place in unit time.

11. This view may be taken of salts in solution, that the bonds of attraction connecting the "ions" together are lengthened by the solvent. When the length of the Faraday tubes is below a certain critical length, the salt is non-ionized. When the average length of the tubes of force is equal to or a little less than the critical length, a few interchanges of ions between adjacent molecules take place, and the salt is partially ionized. When the length of the Faraday tubes is greater than the critical value, then perfectly free interchange takes place between the ions of different molecules, and the salt is completely "ionised." *W. D. B.*

The ultra-violet absorption spectra of aromatic compounds. *E. C. C. Baly and J. N. Collie. Jour. Chem. Soc., 87, 1332, 1347, 1355 (1905).*—Benzene presents seven absorption bands, the formation of which may be accounted for by there being seven, and only seven, possible different types of making and breaking linkings produced by the internal motions of the benzene molecule.

The introduction of a single substituent group modifies the absorption spectrum of benzene, different types of absorption being produced according to the nature of the substituent group.

Under the conditions of the experiments the mono- and di-hydric phenols are tautomeric substances in the sense that the phenolic hydrogen atoms are in the labile state. This tautomerism is also present in the aminophenols. The absorption produced by this tautomerism is situated in very nearly the same spectra regions as the absorption bands which had their origin in the benzenoid structure of these compounds. It is therefore not possible to determine the presence or absence of a labile hydrogen in the phenols merely by comparing the absorption spectra of the phenols with their methyl or ethyl ethers.

In the derivatives of benzene with two saturated substituent groups, the absorption curve of the para-compounds shows either more bands than the ortho- and meta-compounds or the same number of bands with a much greater persistence. It may, therefore, be considered as the most symmetrical of the three. *W. D. B.*

THE ABSORPTION OF PHOSPHATES BY SOILS[1]

BY OSWALD SCHREINER AND GEORGE H. FAILYER

The minerals in the soil determine the character and, to a certain extent, the amount of the mineral constituents in the soil solution. The concentration, as will be shown in the following pages is, however, largely dependent on the absorptive power of the soil. It has long been known that soils have the power to absorb from solution mineral constituents in considerable amounts, and it is, therefore, highly probable that synthetic as well as destructive processes are taking place in the mineral species of the soil. The well-known experiments of Way, Liebig, Heiden, Knop, Eichorn, Rautenberg, Peters, Voelcker, King, and others have established the general fact that arable soils show a selective absorption toward different mineral constituents. In view of the importance of this subject to a proper understanding of the chemistry of the soil and of soil solutions, a systematic study of the behavior of several soil types toward phosphates has been made. The absorption of phosphate has been especially studied in the light of its influence in maintaining the concentration of this important plant food constituent in the soil moisture. The phosphatic minerals of the soil yield and appear to continue to yield a solution of a concentration which approaches equilibrium between the solution and the solid. As actual equilibrium is probably never realized under such conditions, the concentration is influenced by the amount of surface exposed to the action of the soil moisture during a limited period of time. This concentration in phosphate (PO_4) appears to be constant for any given soil and is dependent on the nature of the minerals in the soil, whether they are readily acted upon by water, carbon dioxide, or

[1] Published by permission of the Secretary of Agriculture.

other substances dissolved in the soil moisture, and on the absorptive capacity of the soil. The magnitude of the absorption together with the removal of the absorbed material from the soil makes it highly probable that the concentration of the constituents of the soil moisture is largely controlled by the absorptive power of the soil. If the concentration of the soil solution in phosphate, for instance, is reduced through any cause, such as removal of phosphate by plants, or influx of rain water, the tendency will be to restore the original concentration by more of the absorbed phosphate of the soil entering into the free soil moisture. If, on the other hand, the phosphate content of the soil moisture be increased above the concentration natural for the extract from that soil, as for instance, by the application of a soluble phosphatic fertilizer or the evaporation of soil moisture, the concentration will be reduced by absorption to the original concentration. This is shown by the following experiments on the absorption of phosphate, the removal of the absorbed phosphate, and the removal of the phosphate originally in the soil. The concentration of phosphate in the solution is maintained with much persistence, although only a small amount of the absorbed phosphate has been removed, thus indicating that while the absorbed phosphate is apparently rendered insoluble, it is nevertheless slowly but constantly going into the soil moisture.

For this absorption study four soil types were used, the Cecil clay, the Penn loam, the Podunk fine sandy loam, and the Norfolk fine sand[1]. The sample of Penn loam was not typical and had rather the texture of a clay loam.

These four soils were subjected to a thorough study, both as regards the absorption of phosphate and the removal of the absorbed phosphate by water. This was accomplished by passing the solution, or water, continuously through the soil con-

[1] For a detailed description of these soil types, see the following: Soil Survey of the Statesville Area, North Carolina; Soil Survey of the Leesburg Area, Virginia; Soil Survey of the Connecticut Valley; and Soil Survey of Prince George County, Maryland, Bureau of Soils, U. S. Department of Agriculture.

tained in a filtering tube especially devised for this purpose, in which the rate of flow of the liquid through the soil was entirely under control.

Description of the Apparatus

The apparatus used is shown in Figure 1. The short filter tube A is made by cutting off the lower part of a Pasteur-Chamberland filter tube and plugging the open end with a rubber stopper. The object in cutting down the filter tube is twofold, first to decrease the filtering surface so as to make it possible to thoroughly control the flow by the device to be described presently, and second, to have the filtering surface as low as possible, so that the solution must pass through the entire soil column. This might be more effectually accomplished by the use of filtering discs, but no filtering material could be found which was suitable for this work. The filter tube was cut so as to leave about 2 cm of the tube projecting above the rubber stopper which holds it firmly in position in the metallic tube B, serving as the receptacle for the soil. The metallic tube is closed at the upper end with a two-hole rubber stopper provided with two glass tubes. One of these tubes is about six feet in length, the end being connected with a funnel. If a greater pressure than six feet is necessary for forcing the liquid through the soil, a piece of tubing is readily added and any desired pressure obtained. A height of more than six feet was, however, necessary in only a single case in the course of these experiments. The shorter tube provided with a rubber tube and pinch-cock serves to let out the entrapped air from the tube when starting the apparatus.

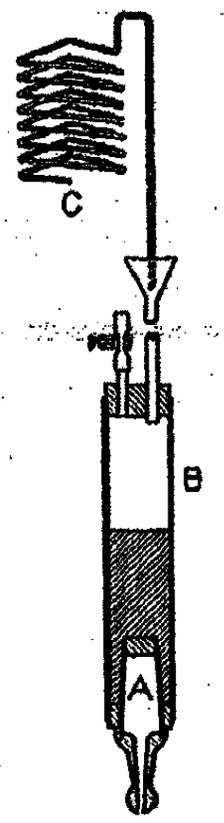


Fig. 1. Showing the apparatus used in the absorption experiments. A, unglazed porcelain filter; B, metallic tube; C, constant dropping siphon.

The rate of flow of the liquid through the soil is controlled

by means of the glass spiral siphon, C. This consisted of thin-walled capillary tubing and was taken of such a length that the friction of the liquid passing through it gave the desired rate of flow. The spiral was suspended in the solution to be used, contained in a beaker of considerable diameter, so that the level of the liquid was not materially changed over night by the flow through the siphon. It was found that the rate of flow was not sensibly affected by slight changes in the height of the liquid in the reservoir. Devices like the Mariotte constant-level bottle were also tried but the rate required was so slow that no satisfactory flow of liquid could be maintained. The length of the spiral was adjusted so that about 50 cc passed in twenty-four hours.

The apparatus may be charged by putting about 50 cc of water or of the solution to be used into the percolating tube and then adding the finely powdered soil in such a way as to prevent trapping of air, or the soil may be made into a thin paste with the solution and this poured into the tube. The latter is then set in a vertical position in a stand, and connected with the rest of the apparatus by inserting the rubber stopper. The pinch-cock is opened and some of the liquid poured into the funnel until the metallic tube is entirely filled. The pinch-cock is then closed and the remainder of the pressure tube filled with liquid by pouring into the funnel. The constant-dropping spiral is then put in position as shown in the figure, and covered to prevent evaporation. The pressure of the column of liquid in the tube forces the solution through the soil and through the filter A, and if the rate of filtration is greater than the rate with which the liquid is supplied by the constant-dropping spiral, the height of liquid in the glass tube will decrease until the pressure of the column of liquid is sufficient to force the liquid through the filter at the same rate as it is supplied by the dropping siphon. If subsequently the filtration should tend to become slower than this rate, the column of liquid in the tube will rise and the consequent greater

pressure will be sufficient to keep the rate of filtration constant and identical with that of the dropping spiral. The apparatus becomes, therefore, perfectly automatic as far as the rate of flow of the liquid is concerned. It is, of course, necessary that the filter be sufficiently close-grained, a condition easily obtained with the filters mentioned, and that the filtering surface be sufficiently small, so as not to filter faster than the desired rate without the application of some pressure.

Removal of Phosphate by Water

A study of the absorption of phosphate by soils from aqueous solutions and the removal of the absorbed phosphate by water, requires a definite knowledge as to the behavior of the phosphate originally in the soils toward the solvent action of water under the identical conditions used in the absorption experiments.

For this purpose the above apparatus was used and the tubes were charged with 100 grams of soil. Pure distilled water was allowed to flow through the soil at the rate of 50 cc in twenty-four hours. The percolate was collected in fractions and the phosphate concentrations determined colorimetrically[1]. The results obtained with the clay soil are given in Table 1. In the first column is given the total number of cubic centimeters of the solution that have passed through the soil, the concentrations in phosphate of the separate fractions being given in the second column. In the third column is given the total amount removed by the water from the soil in the tube, the results being expressed in terms of parts PO_4 per million parts of the soil. It will be noticed that after the first portion, which is considerably stronger than the others, has passed, the solution has practically reached a definite concentration in phosphate. The results with the other soils were very similar. In the case of the clay loam the concentration was

[1] Colorimetric, Turbidity, and Titration Methods, Phosphate I, p. 42, Bull. 31, Bureau of Soils, U. S. Department of Agriculture, 1906.

TABLE I

Removal of phosphate from a clay soil by water

Total cc. of percolate	P.p.m. PO_4 in solution	Total p. p. m. PO_4 extracted from soil
40	26	10
130	8	18
170	8	21
260	8	28
360	7	35
540	6	45
590	6	48
640	6	51
690	7	55
740	5	57
790	7	61
850	7	64

likewise greatest in the first portion (19 p. p. m.) diminishing with succeeding portions, although the drop is not so abrupt as with the clay soil, until again a constant concentration of solution (about 6 p. p. m.) was obtained. With the fine sandy loam the same tendency to yield a solution of constant concentration in phosphate (about 20 p. p. m.) was shown, although this concentration is considerably higher than in the solutions obtained from the other soils. The results obtained with the fine sandy soil were similar to those already given (6 p. p. m.), the first percolate containing 16 p. p. m. The general tendency of the soils is therefore to yield more concentrated fractions at the start but soon to give a solution of nearly constant concentration in phosphate for each soil examined. The higher concentration obtained at the start is very interesting, especially in the light of some of the absorption phenomena to be described farther on in this paper. To ascribe this to the existence of more readily soluble phosphates in the soil which are quickly leached out seems not to be tenable in view of the great absorptive power of these soils for phosphate, even when introduced as an exceedingly soluble salt. The greater concentration in

the first portions seems rather to be connected with the air-dried conditions of the soil. It has been demonstrated that oven- and air-dried soils yield a greater amount of soluble salt to water than do the same soils in the moist field condition.[1] As will be pointed out more explicitly later on, this greater concentration in the phosphate in the case of the dried soils may be at least in part owing to the lower absorptive power of the soil when used in the dry form.

Absorption of Phosphate by Soils from a Solution of Monocalcium Phosphate

The phosphate used in these experiments was the monocalcium phosphate, $CaH_4(PO_4)_2$, as this is the most soluble of the phosphates of calcium and also the one occurring in the superphosphate fertilizers. A solution containing 200 parts of PO_4 per million of the solution was prepared by diluting a stronger solution which had been standardized by gravimetric analysis.

In these experiments the samples of soils used in the previous experiment with the water percolation were studied. The tubes of soil were allowed to drain thoroughly. The apparatus was then filled with the above 200 p. p. m. PO_4 solution as already described under the water percolation. The volume of water or rather soil solution remaining in the apparatus must necessarily have been less than 50 cc and this amount of percolate was discarded at the beginning of the flow of the solution through it. The flow was maintained at a rate of about 50 cc in twenty-four hours. Fractional percolates were collected and the phosphate determined colorimetrically. The results obtained with the clay soil are given in Table 2. In the first column is given the total volume of the phosphate solution which has passed through the soil, and in the second column the concentration of phosphate in the separate portions. The third column gives the amount of phosphate absorbed by the soil, expressed in parts per million. In the fourth

[1] Bull. 22, p. 42, and Bull. 26, p. 55, Bureau of Soils, U. S. Department of Agriculture.

column are given the results calculated by means of a formula derived by certain theoretical considerations which will be developed later. The other columns give the intermediate data used in deriving these calculated results. It will be seen from the table that the removal of phosphates from the solution is almost complete in the first 400 cc passed, the concentration having been reduced from 200 p. p. m to 6 and 8

TABLE 2

Absorption of phosphate by a clay soil from a solution of monocalcium phosphate containiug 200 p. p. m. PO_4

Total cc. of percolate v	P. p. m. PO_4 in solution	Total p. p. m. PO_4 absorbed by soil y obs.	$\log (A-y) = \log A - Kv$ $A = 5500$ $K = 0.000158$				
			y calc.	$(A-y)$	$\log (A-y)$	$\log (A-y)$ calc.	$(A-y)$ calc.
250	6	480	480	5020	3.701	3.701	5020
410	8	790	740	4710	3.673	3.678	4760
570	12	1090	1020	4410	3.644	3.651	4480
780	31	1450	1350	4050	3.607	3.618	4150
1030	58	1800	1720	3700	3.568	3.578	3780
1330	84	2150	2100	3350	3.525	3.531	3400
1660	101	2470	2480	3030	3.481	3.480	3020
2060	115	2800	2880	2700	3.431	3.418	2620
2510	108	3220	3270	2280	3.357	3.348	2230
2820	111	3440	3510	2060	3.314	3.298	1990
3260	127	3760	3810	1740	3.240	3.228	1690
3640	142	3980	4030	1520	3.182	3.168	1470
3890	150	4100	4160	1400	3.146	3.128	1340
4290	152	4300	4330	1200	3.079	3.066	1170
4640	156	4450	4480	1050	3.021	3.009	1020
5000	162	4590	4600	910	2.959	2.952	900
5370	158	4740	4720	760	2.881	2.894	780
5740	169	4860	4820	640	2.806	2.833	680

p. p. m., practically the concentration yielded by the percolation of pure water through the soil. As more solution flows through the soil the concentration of phosphate in the percolate increases, rapidly at first and then more slowly. The absorption is still going on to a considerable extent even after

the passage of nearly 6 liters of the solution and a total absorption of nearly 5,000 p. p. m. of phosphate by the soil. The amount absorbed by the soil as shown in the third column increases rapidly at first and then more slowly as the total amount already absorbed increases. The remaining columns of figures will be discussed presently.

The results obtained with the other soils were very similar. In the case of the clay loam the concentration of the first portions of percolate was very low (5 and 6 p. p. m. for the first 200 cc), approximately that obtained by the action of water on the soil (6 p. p. m.). The concentration of the percolate increased when more solution was passed through the soil, but much more rapidly than in the case of the clay soil. The concentration when about 4 liters of solution had passed through the clay loam was appreciably greater (about 187 p. p. m.) than when nearly 6 liters of solution had passed through the clay soil (about 169 p. p. m.). The amount absorbed by the clay loam when any given volume of solution had passed through it, was considerably less than that absorbed by the clay soil. With the fine sandy loam the concentration of the first fraction of percolate was 22 p. p. m., again agreeing with that of the solution obtained from the soil by percolation with pure water. The amount absorbed by the soil was, moreover, less throughout than that absorbed by either the clay loam or clay soil. The absorptive power of the fine sandy soil was considerably less than that of the soils already considered, as was shown by the relatively higher concentration of phosphate in the percolates throughout. This lower absorptive power of the soil is also shown by the fact that the concentration of the first fractions (19 and 20 p. p. m.) were higher than the concentrations obtained by percolating water through the soil (6 p. p. m.), while with the other soils they were approximately the same as the aqueous percolates from the soils.

Removal of Absorbed Phosphate by Water

At the conclusion of the absorption experiments described in the preceding section the tubes with the soils were allowed

to drain thoroughly and then the apparatus was filled with distilled water in the manner already described. The flow of water was again at the rate of about 50 cc in twenty-four hours, the percolate being collected in fractions and the concentration of phosphate determined colorimetrically as before. The results obtained with the clay soil are given in Table 3. The

TABLE 3
Removal of absorbed phosphate from a clay soil by water

Total cc. of percolate	P. p. m. PO_4 in solution	Total p. p. m. PO_4 remaining in soil
—	—	4860
100	127	4730
230	85	4630
440	55	4510
580	41	4450
730	36	4410
910	32	4350
1140	27	4290
1330	21	4250
1750	21	4160
2280	20	4050
2590	19	3990
2970	16	3930
3370	16	3870
3870	11	3810
4450	8	3760
5030	7	3720
5450	8	3690
5870	7	3660
6300	7	3630

first and second columns give the volume of the solution which has passed through the soil and the concentrations of the separate fractions as before. At the head of the third column is given the total amount of the phosphate absorbed by the soil in the previous experiment and following this are the amounts of absorbed phosphate still remaining after any given volume of solution has passed through the soil. It will be noticed that the concentration of the first fractions is very

high. The concentration in phosphate then decreases, rapidly at first and then very slowly until at about four liters the concentration of the solution has become sensibly constant and is practically the same as that found at the beginning of the absorption and that of the aqueous percolate obtained from the original soil, although the amount of absorbed phosphate still remaining in the soil is nearly 3800 p. p. m., or approximately 75 percent of the total phosphate absorbed. The results with the clay loam showed a similar tendency. The high concentration in phosphate in the first portions gradually gave place to lower concentrations until at about 5 liters the concentration reached was that of the solution obtained at the start of the absorption or by percolating water through the original soil. The amount of absorbed phosphate still in the soil was considerable, however, at this point, approximately 65 percent of the total phosphate absorbed. With the fine sandy loam a concentration of phosphate in the solution approximately equal to that of the first fraction in the absorption experiments, or that of the solution obtained by percolating water through the original soil, was found to be reached when about 3 liters of percolate had been obtained. The amount of absorbed phosphate still remaining in the soil at this point was approximately 60 percent of the total quantity absorbed. The concentration of the solution in phosphate decreases, however, until it falls considerably below (10 p. p. m.) that of the solutions obtained by percolating water through the original soil (20 p. p. m.), although there is present a much larger amount of phosphate in the soil at this stage than there was in the original soil. The Podunk fine sandy loam used in these experiments contained minerals which were appreciably acted upon by water. The percolation of over 40 times its weight of the calcium phosphate solution, containing 42 p. p. m. Ca in addition to the 200 p. p. m. PO_4, together with the subsequent washing with over 60 times its weight of water has produced chemical changes in the soil itself so that we have no longer the identical soil

started with. In so far as the solubility of the phosphate in the soil is concerned, this must be the conclusion reached from the experimental results.

In the case of the fine sandy soil, the concentration of the phosphate in the fractions of percolate decreased rapidly at first and then very slowly, running off to a practically constant concentration toward the end, which is considerably lower than the first fraction obtained in the absorption experiment, but is approximately the concentration obtained from the original soil by percolating water through it, although the amount of phosphate present in the soil is considerably greater.

Absorption of Phosphate from a Solution of Disodium Phosphate and Removal of the Absorbed Phosphate by Water.

In the following experiments a solution of disodium phosphate was used instead of the monocalcium phosphate of the previous experiments. The solution used contained 200 parts of PO_4 per million of the solution and was prepared by diluting a strong solution which had been standardized by gravimetric analysis. The same clay soil, clay loam, fine sandy loam, and fine sandy soil were used as in the experiments with calcium phosphate. The apparatus was charged by putting some of the solution into the percolating tube and then adding the dry soil. The tube was then completely filled with solution in the manner already described and all other operations were exactly the same as in the preceding experiments. The absorption was not carried so far as in the experiments with the calcium phosphate.

In Table 4 are given the absorption results with the fine sandy loam. As before, the fourth column gives the amount calculated by a formula to be discussed later, and the remaining columns give the data used in the calculation and will be discussed presently. It is at once apparent from the second column giving the concentration of phosphate in the separate percolates that the result is different from that obtained when the wet soil was treated with the solution of monocalcium phosphate. The concentration of phospate instead of being low at the very start

and then gradually rising, is in this case quite high at first, rapidly dropping down to a low concentration and then rising gradually. This high concentration at the start is largely owing

TABLE 4

Absorption of phosphate by a fine sandy loam from a solution of disodium phosphate containing 200 p. p. m. PO_4

Total cc. of percolate v	P. p. m. PO_4 in solution	Total p. p. m. PO_4 absorbed by soil y obs.	$\log (A-y) = \log (A-y_o) - K(v-v_o)$ $A = 1100$ $y_o = 170$ $K = 0.000680$ $v_o = 280$					
			y calc.	$v - v_o$	$A - y$	$\log (A-y)$	$\log (A-y)$ calc.	$(A-y)$ calc.
50	175	10	—	—	—	—	—	—
280	130	170	170	0	930	2.968	2.968	930
330	48	250	240	50	850	2.929	2.933	860
380	62	310	310	100	790	2.898	2.900	790
470	72	440	410	190	660	2.819	2.839	690
580	101	540	520	300	560	2.748	2.763	580
680	105	640	600	400	460	2.663	2.696	500
780	143	690	680	500	410	2.613	2.628	420
940	152	770	770	660	330	2.518	2.518	330
1090	167	810	840	810	290	2.462	2.420	260
1320	165	890	920	1040	210	2.322	2.265	180
1480	174	940	960	1200	160	2.204	2.155	140
1700	174	1000	1000	1420	100	2.000	2.000	100
1860	176	1030	1020	1580	70	1.845	1.896	80
1960	195	1040	1030	1680	60	1.778	1.829	70

to the more rapid movement of the liquid through the soil while regulating the flow in the beginning, but the smaller absorptive power of the dry soil when first brought into contact with the solution may be in part the cause. The last results in the second column indicate that the soil is approaching a saturated condition although only about 1000 p. p. m. have been absorbed. This is a much lower absorption than in the case of the monocalcium phosphate with the same soil. When the 1040 parts per million of soil had been absorbed the drained soil was treated with water in the manner previously described. Table 5 gives the results for the removal of the absorbed phosphate. The second column indicates very strikingly the simi-

TABLE 5

Removal of absorbed phosphate from a fine sandy loam by water

Total cc. of percolate	P. p. m. PO_4 in solution	Total p. p. m. PO_4 remaining in soil
—	—	1040
130	165	820
290	111	650
400	32	610
500	26	580
620	23	560
750	20	530
920	16	510
1010	14	490
1110	13	480
1240	13	460
1340	15	450
1470	15	430

larity in the removal of the absorbed phosphate of the soil to the results obtained in the preceding series. Here again the concentration of the solution runs rapidly down until about 900 cc have passed when the concentration becomes practically constant, and comparable with that obtained when monocalcium phosphate was used. The absolute concentration is, however, slightly higher, showing that in the case of this soil the removal as well as the absorption of the phosphate is different when sodium phosphate is used from the results obtained when monocalcium phosphate is applied. As in the preceding series the amount of absorbed phosphate remaining in the soil when this constant concentration of the soil solution is reached is still large.

The results obtained with the clay and clay loam were very similar to those obtained with the fine sandy loam, the concentration of the solution rapidly decreasing to a very low value and then gradually rising. The passage of the solution was exceedingly slow in the case of the clay loam and a considerable length of tubing had to be added to the apparatus in order to

secure the necessary pressure for forcing the solution through the soil. For this reason the experiment was stopped when only about 1200 p. p. m. of PO_4 had been absorbed by the soil. The percolate was far from showing a saturated condition for the soil. An attempt was, nevertheless, made to study the removal of the absorbed phosphate by water, but when approximately 600 cc had passed, the pressure necessary for filtration became so great that the experiment could not be continued in the apparatus used. The clay soil was likewise treated with water when it had absorbed only about 1500 p. p. m. and was still far from showing a saturated condition. The results for both soils show the same general tendency as in the experiments with the monocalcium phosphate where the soils were nearly saturated with phosphate. It would seem, therefore, that the washing out process of the absorbed phosphate is essentially the same in kind, whether the soil has absorbed a large or small amount of phosphate.

The results on absorption and removal of the phosphate for the fine sandy soil were very similar to those for the fine sandy loam. This soil, like the fine sandy loam, approached saturation at a much lower phosphate content than was the case with the monocalcium phosphate. The removal of the absorbed phosphate is similar to the removal from the other soils, a practically constant concentration (8 to 9 p. p. m.) being reached when about 1200 cc have passed through the soil. This concentration is nearly the same as in the case of the monocalcium phosphate.

Graphical Representation and Discussion of the Results

The results obtained in the foregoing experiments on the absorption of phosphate from a solution of monocalcium phosphate, together with those obtained in removing the absorbed phosphate are shown graphically in the following figures. In Figure 2 are shown the results obtained with the solutions. The abscissas represent the liters of solution or of water which have been passed through the 100 grams of soil in the percolating tube.

The ordinates give the concentration of phosphate in the percolate. The upper boundary line of the figure represents the strength of the solution before passing through the soil; the break in each of the curves shows the point where the 200 p. p. m. solution was replaced by distilled water and the washing out of the absorbed phosphate begun. The intercept of each of the curves on the axis of ordinates gives the concentration of phosphate in the solution obtained by percolating water through the original soil. The curves given in this figure are smoothed curves; the experimental points are not given in the diagram as the large number and intermingling of the points would be very confusing. The curves, however, represent very well

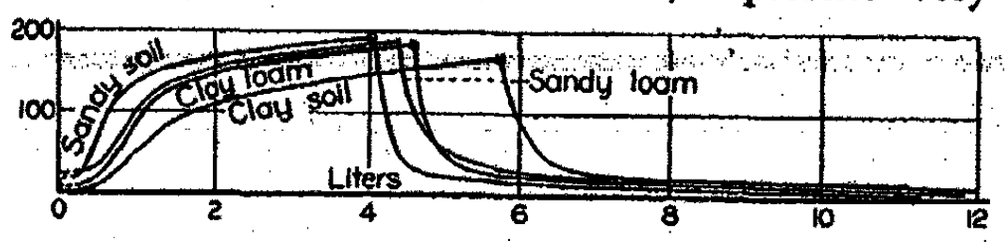


Fig. 2

Solution Curves. Absorption of phosphate by soils from a solution of monocalcium phosphate and the removal of the absorbed phosphate by water.

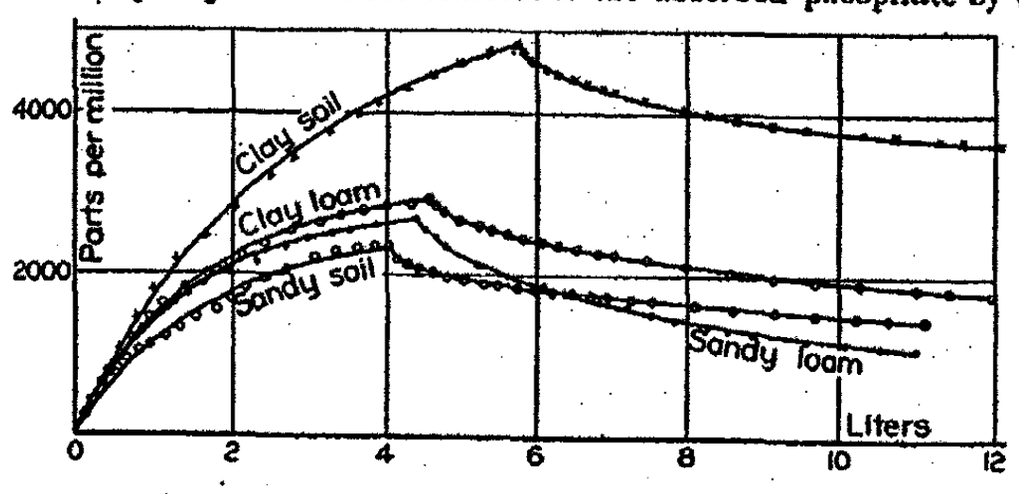


Fig. 3

Soil curves. Absorption of phosphate by soils from a solution of monocalcium phosphate and the removal of the absorbed phosphate by water.

the general facts brought out by the figures. It will be noticed that the absorption of phosphate from the solution by the soil is considerable for the first 300 cc of the solution passed, the concentration of the solution being reduced approximately to that of the soil extract obtained from the original soil. After this the curves rise with increasing amount of solution

passed, quite rapidly in the case of the sandy soil, and much more slowly in the case of the clay soil. All the curves approach the line representing the concentration of the original solution, namely, 200 p. p. m., apparently as an asymptote. The curves for the removal of the absorbed phosphate show a very decided drop at the start and then rapidly tend to become horizontal when concentrations approximating those of the water extract of the original soil and those of the first few fractions of percolate in the absorption experiments have been reached, as is shown by comparing the extremes of the curves. It is, moreover, significant that the soils give, after this absorption treatment, solutions which are much nearer alike in concentration of phosphate than did the original soils, although the amounts of phosphates in the soils are in all cases greater than those originally present. The concentrations at both ends of the curves are practically identical in the case of the sandy soil, clay loam, and clay soil studied, but in the case of the sandy loam the concentration is even less than that of the aqueous extract of the original soil.

In Figure 3 are shown the results on the basis of the soil itself, the abscissas being the liters of solution passed, as before, and the ordinates the parts of phosphate absorbed per million parts of soil. It is at once apparent that the absorption curves of the different soils are quite similar in character although these soils differ in the amount of phosphate absorbed. At about 2400 p. p. m. the curve for the sandy soil indicates a rapid approach to a horizontal position, that is, to a condition of saturation for phosphate, whereas the curve for the clay soil at about twice the height is still showing a decided tendency to rise. The curves for the removal of the absorbed phosphate drop rapidly at first and then run smoothly and gradually downward. The removal curve for the sandy loam has a greater slope than the others, which fact is, of course, also shown by the higher concentration of phosphate in the solution as appears from Figure 2. A comparison of the two figures also shows very

strikingly that with all the soils studied a solution of low phosphate content, approximately the strength of the extract obtained from the original soil, is obtained when only a fractional part of the absorbed phosphate has been removed.

The above graphical representations of the absorption results indicate, as has already been pointed out, that the soils are approaching saturation for phosphate under the conditions of the experiment, as is shown by the fact that each curve is evidently approaching a horizontal asymptote. It has been found that these absorption phenomena are quite accurately represented by an expression of the same form as monomolecular reaction velocities, rates of solution, and other analogous processes. Lagergren[1] has already shown that the rate of absorption of several organic acids by charcoal in respect to time, behaves like a monomolecular reaction.

If we represent the maximum amount which the soil can take up by A, that is, the ordinate of the asymptote mentioned above, and let y equal the p. p. m. PO_4 it has taken up when the volume v has passed through the soil, the simplest assumption that can be made is that the amount absorbed from a unit volume of solution as it passes through the soil is proportional to the amount the soil can still take up. This assumption may be represented by the differential equation

$$\frac{dy}{dv} = K(A - y) \tag{1}$$

or

$$\frac{dy}{A - y} = K dv$$

which, when integrated, gives

$$\log (A - y) = C - Kv, \tag{2}$$

C being the integration constant. If y_0 is the amount which has been absorbed when the volume v_0 has passed through, we have

$$\log (A - y_0) = C - Kv_0$$

or

$$C = \log (A - y_0) + Kv_0, \tag{3}$$

[1] Bihang till K. So. Vet.-Akad. Handl., 24, Afd. II, No. 5 (1898).

and by substituting this value of C in equation (2) we obtain the equation

$$\log (A - y) = \log (A - y_o) - K(v - v_o), \quad (4)$$

which must be satisfied by the observed values of y and v if the original assumption be correct. If the curve passes through the origin, $y = 0$ when $v = 0$, *i. e.*, $y_o = v_o = 0$, so that the equation reduces to the simpler form

$$\log (A - y) = \log A - Kv. \quad (5)$$

The curves evidently do not pass exactly through the origin, but for a test of the assumption it is sufficient to use the simplified equation (5) instead of the more general equation (4). Since K and log A are constants to be found from the observations, Briggsian instead of Naperian logarithms may be used in the calculations.

The simplest way to test the applicability of equation (5) appears to be, 1st, to find A approximately by inspection of the curve obtained by plotting the experimental data; 2nd, to make from the observed values of y a table of log $(A - y)$; 3rd to make a plot using v as abscissa and log $(A - y)$ as ordinate. Since equation (5) is that of a straight line, the plot will be a straight line, if the correct value for A has been chosen, if there are no observational errors, and if the assumption regarding the form of the differential equation really represents the facts. The intercept on the axis of ordinates will then be log A and the negative slope of the line will be the constant K. In carrying out this process, the value selected for A fixed the point where the line must cut the axis of ordinates, *i. e.*, its intercept or log A. The problem, therefore, was to find by trial such a value for A as would make all the points, whose abscissas were v and whose ordinates were log $(A - y)$, lie most nearly on a straight line through this starting point.

The monocalcium absorption results for all of the soils studied have been tested in this way, and it has been found that a fair agreement with equation (5) is obtained when the following constants are used:

	A	log A	K
Clay soil	5500	3.740	0.000158
Clay loam	3100	3.491	0.000267
Sandy loam	2800	3.447	0.000299
Sandy soil	2600	3.413	0.000247

The results obtained by using these values in calculating the p. p. m. PO_4 absorbed by the clay soil for any given volume of solution which has percolated through it are given in the fourth column of Table 2. The results observed with the other three soils were treated in the same manner, using the constants given above for the respective soils. The calculated and observed values for y are given in Table 6. In Figure 3 the

TABLE 6

Absorption of phosphate by soils from a solution of monocalcium phosphate. Results expressed as parts PO_4 per million parts of soil

Clay loam		Fine sandy loam		Fine sandy soil	
y obs.	y calc.	y obs.	y calc.	y obs.	y calc.
220	200	260	290	250	210
420	390	500	500	480	400
650	610	740	740	660	530
990	940	1040	1010	850	700
1200	1120	1320	1250	950	850
1460	1370	1490	1450	1050	980
1640	1550	1660	1650	1120	1100
1830	1810	1750	1780	1210	1260
2000	2000	1890	1920	1320	1400
2080	2130	2020	2080	1440	1540
2210	2280	2140	2250	1540	1660
2360	2420	2330	2370	1690	1760
2530	2550	2460	2450	1820	1870
2630	2650	2500	2510	1930	1960
2720	2720	2530	2560	2050	2060
2790	2780	2600	2610	2230	2150
2830	2850	2640	2640	2290	2210
2860	2900	2690	2670	2320	2270
2920	2910	——	——	2340	2310
——	——	——	——	2350	2340

absorption curves are drawn through the calculated points, and the experimental points are indicated by the specific signs. The curves show, therefore, how well the calculated and observed results agree. A much closer agreement between the calculated and observed values is obtained by discarding the first one or two observed results in the manner to be described presently in the discussion of the sodium phosphate curves, *i. e.*, by using the general equation (4).

Apparently, the removal curves may be represented by a similar formula when the first few points are left out of consideration. This disagreement of the first few points may be owing to the inaccuracy occasioned by the phosphate solution remaining in the soil when the washing process is begun. The equation for the removal of phosphate from the soil may be written as follows:

$$\frac{dy}{dv} = K\,(y - B),$$

where B is the ordinate corresponding to the asymptote of the removal curve, that is, the amount of phosphate which has apparently become permanently insoluble so far as any reasonable amount of solvent passing through the soil is concerned. The calculated results obtained with this equation bring out no information not given by the plotted curves and are, therefore, omitted.

In Figure 4 the results of the experiments with sodium phos-

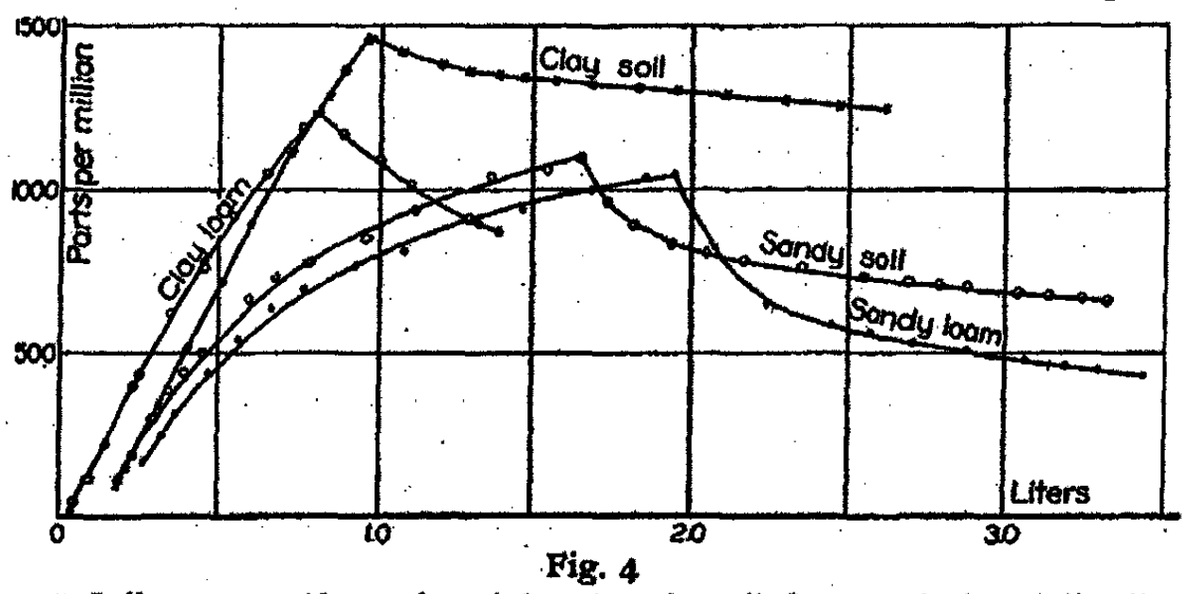


Fig. 4

Soil curves. Absorption of phosphate by soils from a solution of disodium phosphate and the removal of the absorbed phosphate by water.

phate are plotted for the soil. As before, the ordinates represent the amount of phosphate absorbed by the soil and the abscissas the volume of the solution or water which has been passed through it. The break in the curves shows the point where the phosphate solution was replaced by distilled water and the washing out of the absorbed phosphate begun.

It is at once apparent that the sandy soil and sandy loam are approaching a condition of saturation, whereas the curves for the clay and clay soil are still rising rapidly and the soils are obviously far from saturation for phosphate. The apparently greater absorption by the clay loam is entirely due to the different starting points of the curves. When the starting points are made to coincide, the clay loam curve lies throughout below that of the clay soil curve, as it did in the case of the monocalcium phosphate. This will be more strikingly brought out by the application of the formula to these curves, when it will be shown that they are described by the same formula which was found to apply in the case of the monocalcium phosphate. There is, however, an actual inversion of the order of the curves in the case of the sandy soil and sandy loam, the latter showing the lower absorptive power in this case, whereas with the monocalcium phosphate it showed the higher absorptive power. Here again the difference between the two curves is much less than it appears to be, for if the starting points of the curves were made to coincide, the curves would lie much closer together. The fact remains, however, that these two soils are showing a relatively different absorptive power with sodium and monocalcium phosphates. That the specific absorptive capacity of both these soils is markedly different in the present series from that in the former series will be shown presently.

The removal curves are in general similar to the monocalcium curves already given. With the almost saturated soils, the drop is rapid at first, but the curves soon descend at a practically constant rate. With the less saturated soils, the initial drop is less marked, but the results show clearly that distilled

water is slowly but constantly removing the absorbed phosphate whether the soil is nearly saturated with phosphate, or whether it is only partially saturated. This latter result was, of course, to be expected, since the phosphate originally in the soils was removed by distilled water at a practically constant rate.

It has been found that the same differential equation represents the absorption curves for the sodium phosphate as for the monocalcium phosphate. It will be observed from the figure that the curves do not pass through the origin so nearly as they did in the case of the monocalcium phosphate. This is owing to the lower absorption at the very start of the experiment, and is due either to the lower absorption of the dry soil used in the present series as compared with the wet soil used in the previous series, or to the too rapid flow of the strong phosphate solution at the start before the apparatus had adjusted itself. Whatever may have been the cause, it is, for this reason, obviously necessary to use the general equation (4) instead of the simplified equation (5) which sufficed for the representation of the results with monocalcium phosphate. This amounts merely to substituting for log A, in the equation

$$\log (A - y) = \log A - Kv,$$

$\log (A - y_o)$, where y_o is the ordinate of the point taken as the first reading, and also substituting the corresponding value of $(v - v_o)$ for v, where v_o is the volume corresponding to the y_o taken as the first reading. The equation then becomes:

$$\log (A - y) = \log (A - y_o) - K(v - v_o)$$

namely, the general equation (4).

It is, of course, impossible to get any idea of the value of the specific absorptive capacity of the clay soil and the clay loam from the two curves given in the figure, as these are far from showing any tendency to approach a horizontal asymptote. A careful examination of the figures, however, shows that the results fall almost exactly on the curve for the results obtained with these same soils by using monocalcium phosphate, when allowance is made for the different starting points of the curves. In other words, the behavior of the clay soil and the clay loam

is very accurately described by using the same values for A as in the case of the monocalcium phosphate, together with the other constants given below:

	A	log $(A - y_0)$	K
Clay soil	5500	3.728	0.000162
Clay loam	3100	3.474	0.000290

The results for the sandy soil and the sandy loam are likewise quite accurately described by the above equation, using the following values:

	A	log $(A - y_0)$	K
Sandy loam	1100	2.968	0.000680
Sandy soil	1200	3.004	0.000669

The results obtained by using these values for the respective soils are given in Tables 4 and 7. In the figure the absorption

TABLE 7

Absorption of phosphate by soils from a solution of disodium phosphate. Results expressed as parts PO_4 per million parts of soil

Clay soil		Clay loam		Fine sandy loam		Fine sandy soil	
y obs.	*y* calc.	*y* obs.	*y* calc.	*y* obs.	*y* calc.	*y* obs.	*y* calc.
90	—	40	—	10	—	110	—
150	150	120	120	170	170	190	190
330	330	220	220	250	240	300	280
510	510	430	430	310	310	380	350
710	710	620	640	440	410	440	410
890	900	760	760	540	520	490	480
1110	1110	910	920	640	600	660	630
1280	1280	1050	1050	690	680	730	700
1360	1370	1180	1170	770	770	770	780
1470	1480	1240	1230	810	840	850	870
—	—	—	—	890	920	930	940
—	—	—	—	940	960	1040	1020
—	—	—	—	1000	1000	1050	1070
—	—	—	—	1030	1020	1090	1090
—	—	—	—	1040	1030	—	—
—	—	—	—	—	—	—	—

curves is drawn through the calculated points, the experimental points being represented by the specific signs. The curves as well as the table show how closely the observed and calculated results agree.

In the following table is given a comparison of the specific absorptive capacities for phosphate found for the four soils when sodium phosphate was used and when monocalcium phosphate was used, together with the constant K. The values of log A and log $(A - y_o)$ may be omitted in the comparison as they depend on the above specific absorptive capacity and the starting point of the curves.

	Monocalcium phosphate		Sodium phosphate	
	A	K	A	K
Clay soil . . .	5500	0.000158	5500	0.000162
Clay loam . .	3100	0.000267	3100	0.000290
Sandy loam . . .	2800	0.000299	1100	0.000680
Sandy soil . .	2600	0.000247	1200	0.000669

It is at once apparent that the phosphate absorption of the clay soil and clay loam studied is the same for the calcium and the sodium phosphates as is shown by the equal values for the specific absorptive capacities for phosphate and for the close agreement for the value of K in both cases. It seems possible that the ferruginous nature to these particular soils is responsible for this similarity in the absorption of the phosphate in the two cases. With the other two soils, however, the result is quite different. The use of the sodium phosphate has changed the specific absorptive capacity of both soils markedly, and also the value of K. It seems probable, therefore, that the sodium and calcium played an important part in the changes which have taken place in these soils.

Bureau of Soils,
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ON AIR LIQUEFIERS

BY F. G. COTTRELL

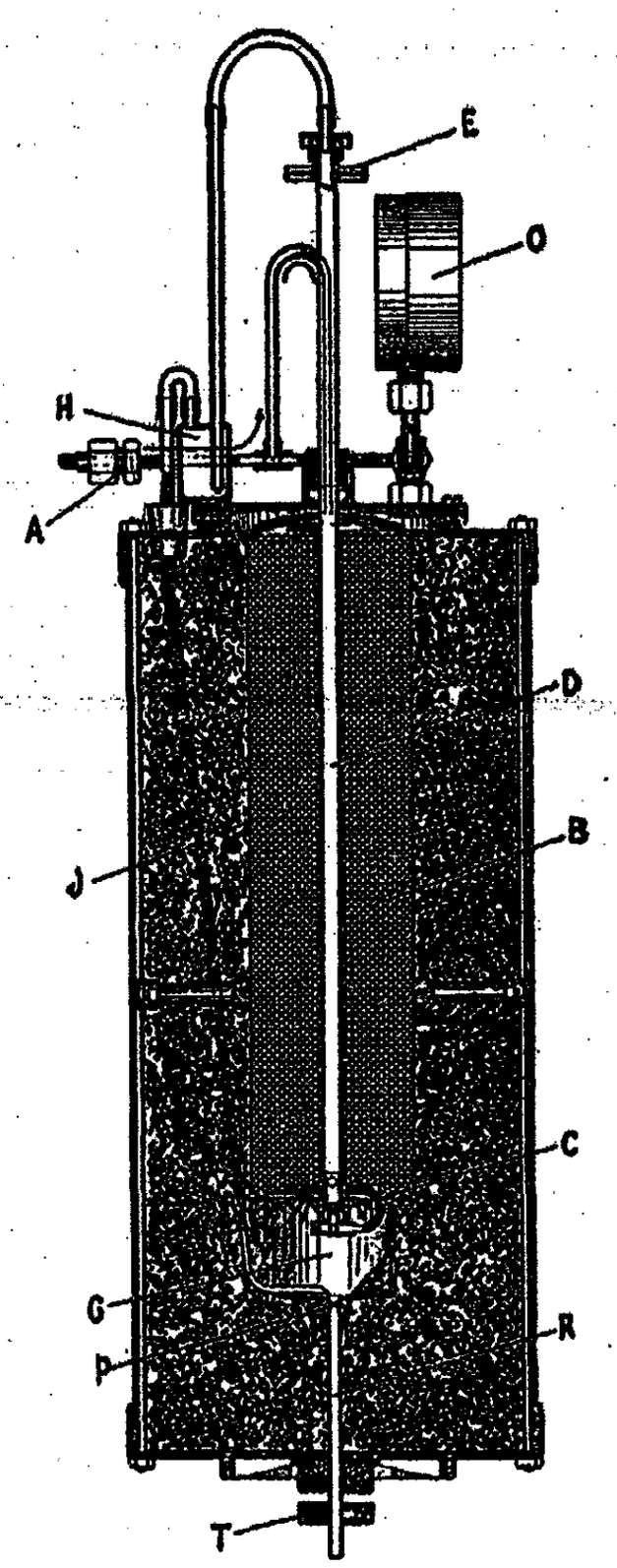
Introduction Note

At the time the following work was undertaken the article by Bradley and Hale cited in the first paragraph below had escaped the author's notice, and in fact it only came to his attention after the experiments here described were completed and a first draft of this article written out. As the present installment represented only the beginning of our original laboratory program and the article above cited suggested much the same general field for investigation, the author, after forwarding this manuscript to the editors, wrote Prof. Bradley outlining what had been already accomplished here and what further work was contemplated and suggested the desirability of some sort of cooperation in the future. Prof. Bradley heartily indorsed this suggestion and further stated that experiments very similar to those here described had been completed some time ago in his own laboratory and with essentially the same results. As the two sets are entirely independent and mutually support each other at least as far as the facts are concerned it has been arranged through the courtesy of the editors of this Journal to publish the two articles simultaneously.[1]

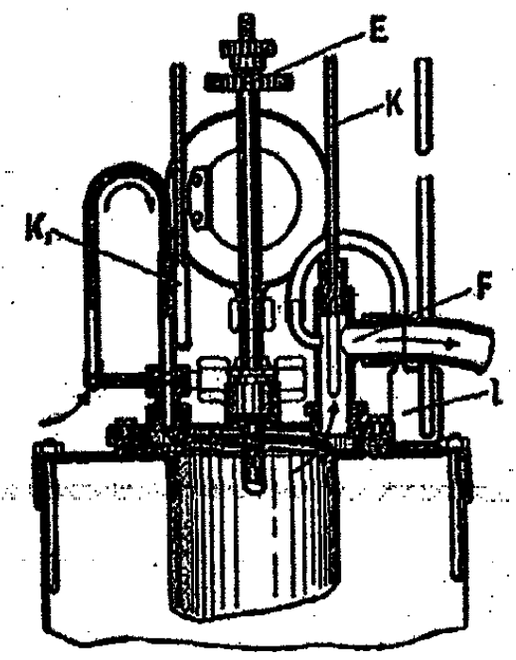
Through the courtesy of Prof. Bradley I have had the opportunity of reading his manuscript while correcting the proof of the present article and feel that the two articles contain no essential contradictions. The inferences which we are disposed to draw may differ somewhat, but as it is hoped that further experiments will remove many of these points it seems hardly expedient to discuss them at present.

I am glad to have this opportunity to express my appreciation of the friendly and courteous spirit with which the authors of the other paper have entered into the present matter.

[1] See article entitled "Precooling in the Liquefaction of Air," by W. P. Bradley and G. O. P. Fenwick, pages 275 to 289 this Journal.



Full length sectional View of Air Liquefier.



Part sectional View of Top of Air Liquefier.

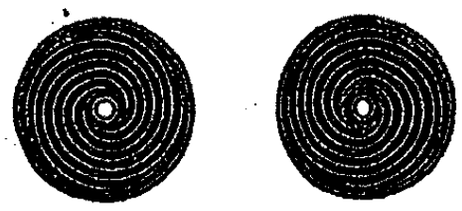


Diagram showing arrangement of Regenerator Coils.

Sectional Views of Air Liquefier.

Fig. 1

The question as to just where and under what conditions liquefaction takes place in air liquefiers of the Hampson and Linde types has of late been raised by several authors. A sum-

mary of the present state of our knowledge together with some very interesting measurements of temperature in the return air current may be found in a paper by Bradley and Hale.[1] The consensus of opinion, which is also supported by the direct temperature measurements in the paper cited, seems to be that in the liquefiers of this type little or no liquefaction takes place before the air reaches the expansion valve.

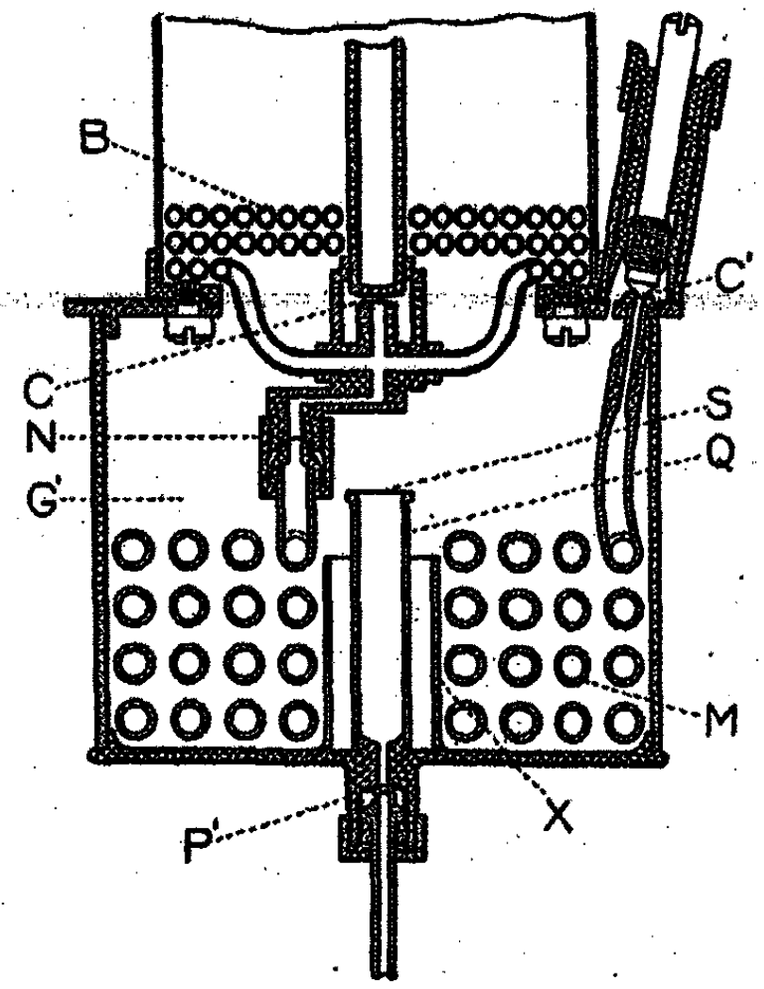


Fig. 2

The efficiency of the apparatus, both while starting up and under steady running conditions, would thus seem to depend wholly upon upon the Joule-Thomson effect. In order to determine what would happen were more complete cooling effected before the air reached the expansion valve the following experiment was undertaken with the liquefier of the Chemistry Department of the University of California. The apparatus is a regular Hampson laboratory type liquefier receiving its air from a four-stage belt-driven air compressor designed and built for

[1] W. P. Bradley and C. F. Hale: Phys. Rev., 19, 387–395, (1904).

the purpose by the Rix Compressed Air and Drill Co., of San Francisco. Fig. 1 represents the liquefier as supplied by the Brin's Oxygen Co.[1] Fig. 2 shows how the liquid reservoir was modified for the experiment in hand. C is the regulating valve on the ordinary liquefier, G the reservoir for the liquid air and B the regenerator coils. For the experiment in hand a large container G′ 8 cm deep by 10 cm diameter was substituted and a coil M of nearly 3 meters of copper tubing 4.5 mm internal diameter and wall 1 mm thick was arranged as shown in the figure in four layers of four turns each, being connected to the main coil of the liquefier by a small brass union N in such manner that the air might be allowed to take its old course through the valve C as usual or be sent through this new coil and escape at the valve C′, both of these valves discharging freely into the reservoir G′. The liquid in this chamber had to rise to the top of the tube Q before it could overflow into this through the wire gauze S and be drawn off through the valve P′, thus ensuring the complete covering of the coil M. The sleeve X perforated with a ring of holes at the bottom was simply to ensure good circulation of the liquid in the chamber G′. Evidently though there may be a question as to the liquefaction of the gas before it reaches the valve C, this can hardly be the case if it is allowed to pass on to C′ before escaping. In fact it should be not only liquefied but reduced in temperature very nearly to its boiling-point at atmospheric pressure which is practically the condition of the liquid in G′.

To test the relative efficiencies of the liquefier in the two forms the compressor was run at a steady rate for about half an hour after the liquid began to flow, *i. e.*, after the lower coil was entirely immersed. The compressor was making about 120 revolutions per minute. The cylinder receiving the free air is 8 inches in diameter with a 6-inch stroke, single-acting. The pressure of the air delivered to the liquefier was held as constant as possible at 200 atmospheres. It was found that it made no appreciable difference through which of the valves, C or C′, the

[1] The cut is reproduced from the company's circular.

air was allowed to escape. Liquefaction took place in either case and the quantity per minute was the same within the limits of observational error. The mean rate of production was in the neighborhood of 2 liters per hour which is a little lower than the regular output with the simple reservoir system, the difference being evidently due to greater losses by conduction of heat from without. The comparisons were for the most part made by drawing liquid every three minutes into a graduated vacuum cylinder, using valves C and C′ during alternate periods. By the arrangement of the valves, described above, the discharge could be shifted instantly from one valve to the other. Continuous runs on one valve extending over several periods were also made. The quantities of liquid for a series of successive three-minute periods all with one valve showed irregular variations among themselves sometimes as high as 3 percent or 4 percent, due to variations in speed of compressor, adjustment of outlet valve, and most important of all, rapidity and other conditions of drawing off the liquid. The difference between runs on the two valves showed no larger variations than those on a single valve and were in favor sometimes of the one, sometimes of the other. Since from the valve C′ it can scarcely be maintained that much gas emerges as such it is evident that in this case at least the Joule-Thomson effect in its ordinary sense nearly disappears. Of course we may have an analogous effect for the slight expansion of the liquid but experimental data as to its magnitude fail us, and it is probably very small. The fact that the performance of the apparatus is sensibly the same with either valve suggests at least a lurking possibility that the same conditions may really occur in the ordinary type of liquefier.

Waiving the question of identity in the two processes it is at least of interest to analyze the new cycle. For this purpose we may best separate it into six parts: (1) Cooling within the pressure tube. (2) Condensation to liquid. (3) The conduction of heat from the inner to the outer wall of the tube; this may be lengthwise of the tube as well as straight through the wall. (4) The passage of the liquid as such through the valve C′. (5)

The evaporation of the liquid without. (6) The warming of the vapor from the external surface of the pressure tube.

Of these it is obvious that (2) is thermodynamically a reversible process; (5) is also reversible in so far as it is not too violent and we may neglect the dynamic factors such as kinetic energy of the gas current. (3) and (4) and to a lesser extent perhaps (1) and (6) are necessarily the irreversible steps of the cycle, and improvements in its practical operation must depend upon reducing their effect to a minimum.

We may turn now to what this suggests as regards the possibility of future improvements in liquefiers of this type. Up to the present the inefficiency of the liquefiers in converting mechanical work, represented in compression, into refrigeration has been laid upon the free expansion at the escape valve and because the return air from the regenerator coils was nearly the same temperature as the ingoing pressure air, it has been assumed that the thermal interchange in these coils is highly efficient. If the liquid is formed before reaching the valve the only loss at this point is due to the friction of the liquid flowing through the valve. This can be readily calculated as it is simply the volume of this liquid multiplied by the difference of pressure on the two sides of the valve, *i. e.*, 200 atmospheres in the above experiment. Assuming the validity of Boyle's law up to this pressure and the density of the liquid as about 1/800 that of air at atmospheric temperature and pressure we find the loss to be about 5 percent of the total energy represented in isothermal compression of the gas.

The fact seems not to have been thoroughly appreciated that the difference in temperature of the ingoing and outcoming air at the top of the regenerator coils is not a complete measure of their thermodynamic efficiency. To define this completely the form of temperature gradient in both currents must be known. Reference to Fig. 3 will serve to make this clear.

A steady state is assumed to have been reached; we further assume that there is no temperature difference between the enter-

ing (pressure) air and returning (free) air[1] and also that the liquefier system is completely insulated as regards direct heat conduction from without. Let the temperature at the outer end of the coil be T_1 and the temperature at the escape valve T_2. Let Q be the heat taken up between T_2 and T from the copper coils by the quantity of free air returned in unit time, Q_1 the special value of Q for $T = T_1$. Further let Q′ be the heat given out between T_1 and T by the quantity of pressure air supplied to the coils in unit time, Q_2' the value of Q′ for $T = T_2$.

The copper wall of the pressure tubing we may consider as an intermediate reservoir of heat. In Curve A of Fig. 3 the ordinates are the temperatures of the returning free air current at different points in its course while the abscissae are $(Q_1 - Q)$.

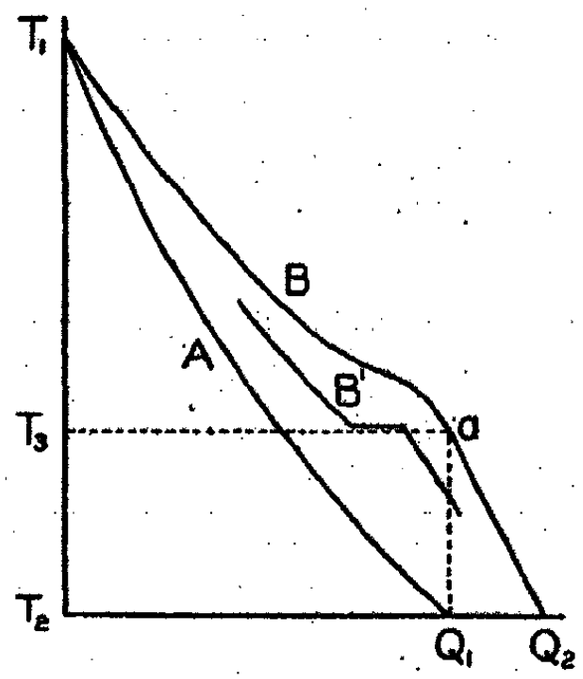


Fig. 3

If the specific heat at constant pressure (C_p) is constant over this range of temperature, A will be a straight line. If it increases with decreasing temperature[2] A will have more the form indicated in the figure, but for our present purpose this matters little. In curve B the ordinates refer to the temperature of the air within the pressure tube and the abscissae are the correspond-

[1] In practice with our regular equipment as described above this difference usually amounts to about 2° C. In tests with an improved liquefier described by Bradley and Rowe (Phys. Rev. 19, 230-343) this is reduced more than tenfold.

[2] See C. v. Linde, Engineer (London), 82, 509, Nov. 20, 1896.

ing values of Q′. Were C_p constant B would start from T_1 as a straight line. The greater the percentage of air liquefied the less Q_1 will be and the greater will be the angle between A and B at T_1. If C_p increases with increase of pressure[1] this will also increase the angle and if C_p varies with temperature, B will cease to start as a straight line. Should we be working with a single gas (*e. g.*, nitrogen) and at a pressure below the critical, the temperature of liquefactiou for the given pressure would be marked by a discontinuity of the type shown in B′. With rising pressure the horizontal part would become shorter and disappear at the critical pressure (probably leaving a point of inflection in its place) and with a gaseous mixture like the air no actual discontinuity would occur at any pressure but simply an inflexion such as shown in B which would flatten out with increase of pressure but need not, and probably does not, entirely disappear even above the critical pressure of all the components of the mixture. The increase of pressure would, of course, also displace this region of the curve steadily toward T_1. The cooling of the ingoing air from T_1 to T_3 is what is accomplished by the return air (specific heat), the remainder of the cooling from T_3 to T_2 is accomplished by the evaporation of that part of the liquid (latent heat) necessary to produce this return air. The distance between the points marked Q_1 and Q_2' represents the amount of heat abstracted from the air which is drawn off as liquid; *i. e.*, it measures the useful output of the process.

The path $T_1Q_2'Q_1T_1$ represents the interchange of heat for the mass of copper tubing considered as a heat reservoir with a given mass of gas passing down the coils under pressure and the corresponding (but not equal) mass of free air returning. The total amount of heat given to and taken from this reservoir is the same, *i. e.*, the integral taken about the whole cycle.

$$\int_{T_1}^{T_1} dQ = 0$$

but the entropy

$$\int_{T_1}^{T_1} \frac{dQ}{T} > 0.$$

[1] See C. v. Linde, Engineer (London), 82, 509, Nov. 20, 1896.

In other words the greater the area enclosed by the above path the greater is the increase in entropy in describing the cycle.

The entropy-temperature diagram will appear essentially the same in form as the heat-temperature diagram, the chief difference being that both curves are more convex toward the origin. In the heat-temperature diagram it is not easy to give an exact and simple physical interpretation to area, but in the entropy-temperature diagram the area corresponding to T_1, a Q_1T_1 has the dimensions of heat and is the equivalent of the work wasted in the interchange of heat in the copper tubes above the reservoir of liquid. The area corresponding to $aQ_1'Q_1a$ gives the waste in the interchange between evaporating liquid and pressure air. Of course the point a may lie above the point of inflection on the curve. If the argument of the present paper is correct it is chiefly in the reduction of these areas that essential improvements in this type of liquefier are to be looked for.

It is interesting to note in this connection that Linde explains the higher efficiency of his system on the grounds that the Joule-Thomson effect is proportional to the difference of pressure $(p_1 - p_2)$ on the two sides of the expansion valve while the work of compression is proportional to $\log \frac{p_1}{p_2}$. He therefore works between two relatively high pressures (200 and 16 atmospheres), instead of one high and one equal to atmospheric as in the Hampson system. This argument is undoubtedly valid as far as starting up the machine is concerned, but once in steady state it would seem from the above that the higher efficiency may quite possibly be due to the curve A approaching curve B. Curve B is, of course, the same in the two systems if working at the same initial pressure.

Linde[1] points out his belief that the Joule-Thomson effect ceases to obey the above law for very high pressures and for this reason appears to look upon 200 atmospheres as approaching

[1] l. c.

the limit of practicability. It would seem, however, that if the Joule-Thomson effect is not the governing factor this question must come up anew.

If we are dealing with reversible processes throughout, the more heat we abstract from the gas before it goes to the liquefier the less will have to be removed from it in that instrument to bring it to a given standard state. An increased initial pressure means more heat removed in the cooling water of the compressor. The possible disadvantage that the increased pressure brings with it is increase in friction at the escape valve. As long as the escaping substance obeys the $pv = RT$ law this friction loss is independent of the pressure, the increase of the latter being exactly compensated for by the decrease of the volume passed. But we have here to deal with a liquid whose compressibility we do not know. At 200 atmospheres as pointed out above, this loss does not exceed 5 percent of the total useful work of compression even if we assume the liquid as incompressible and, even making this latter assumption, doubling the pressure would only double this loss. The other factor of importance in the problem is the change in shape of Curve B which this increase in pressure would produce. It seems certain than any residual flexure left from the critical phenomena would tend to be smoothed out. Beyond this, little can be said at present as the only values for specific heats at these pressures and temperatures appear to be those deduced by Linde[1] from the performance of the apparatus itself.

The experimental work of Bradley and Rowe already referred to points strongly to the conclusion that we have by no means reached the optimum of initial pressure at 200 atmospheres and for small plants, at least, there seems no valid mechanical objection to using higher pressures. Experiments in this line are at present under way in this laboratory. It was the original intention to delay the present paper until definite results in the latter line could be secured, but as the program of the work has grown somewhat and now bids fair to consume more time than

[1] l. c.

originally expected, the liberty is taken of presenting this isolated step in the hope it may prove suggestive to other workers in the same field and encourage cooperation.

Summary

In the present paper it is pointed out that although in the Hampson and Linde liquefiers it may be questioned whether any liquefaction takes place before the gas reaches the expansion valve the output of the Hampson at least is not altered when the coil system is so altered as to ensure complete condensation before release of pressure, thus eliminating the Joule-Thomson effect.

The theory and possibilities of this modified cycle are then discussed.

The question is left an open one as to how closely the older cycle approaches this new one.

The losses in the interchangers (of either system) are discussed.

In conclusion, I wish to express my indebtedness to Mr. Val. Arntzen, mechanician of this department, for the care with which he constructed the apparatus described; likewise to Mr. A. C. Wright, of the Department of Mechanics, for the draft of Fig. 2, and to Dr. T. C. McKay, of the Department of Physics, for friendly criticism of the thermodynamics involved.

University of California,
Dept. of Chemistry,
Berkeley, Nov. 6, 1905

PRECOOLING IN THE LIQUEFACTION OF AIR[1]

BY W. P. BRADLEY AND G. P. O. FENWICK

Since 1902, experimental inquiries have been in progress in this laboratory regarding the factors which affect the efficiency of an air liquefier of the single-circuit type. Some of the results have already been published.[2]

The experiments whose results are embodied in the present paper were completed in June last.[3]

It appears to have been generally assumed, doubtless under the leadership of Linde and Schrötter,[4] that the absorption of heat at the valve of an air liquefier is due to the Joule-Thomson effect.

In the formula adopted by Schrötter, $D = \frac{P_2 - P_1}{4} \frac{(289)^2}{T}$, the fall of temperature, D, at the valve varies inversely as the square of the absolute temperature, T, at which the high pressure air reaches the valve.

Of course the same absorption of heat which manifests itself merely as a fall of temperature, in case no liquid is produced, results in an increased yield of liquid when once the liquefaction temperature is attained. It is clear therefore that in this view of the matter extraordinary emphasis is thrown upon the efficacy of precooling as a prerequisite for efficiency and economy in liquefaction.

[1] Contribution from the Cryogenic Laboratory of Wesleyan University.

[2] Bradley and Rowe: Phys. Rev., 19, 330 (1904); Bradley and Hale: Ibid., 19, 387 (1904).

[3] It was not intended to publish these until the general inquiry should be more advanced. It was learned, however, through the courtesy of Dr. Cottrell, of the University of California, that a similar work had been undertaken by him. Moreover, in the correspondence which followed, it transpired that we had been engaged upon the same specific problem during the last year, and that our results were practically identical. As these seemed of considerable interest, it was agreed to publish them at once and simultaneously. We are glad to express at this time our appreciation of the courtesy shown by Dr. Cottrell in connection with this matter.

[4] Paper read before the Society of German Engineers, 1895. Abstract in the *Scientific American Supplement*, December 21, 1895.

Now there are two general methods of lowering the temperature of the air above the expansion valve in a liquefier which is operated under otherwise uniform conditions. One of these may conveniently be called the external, and the other, the internal method.

External precooling may occur either entirely outside of the liquefier, as is ordinarily the case, or, less commonly, during the passage of the high pressure air through the interchanger. The latter method has been adopted for instance by Olszewski[1] who divides his interchanger and inserts a carbon dioxide-ether bath between the halves.

The internal method of precooling uses for the purpose some of the liquid air which has already been made and is lying in the reservoir of the liquefier.

In connection with the first or external method, a careful analysis of the conditions will be helpful to a clearer understanding of its efficacy.

As has been shown,[2] the temperature at which air enters the top of the interchanger is an exceedingly potent factor in determining the yield of a liquefier. A little consideration however will show that external precooling can never have the full effect which is due from it.

Of course the yield of liquid depends directly upon the temperature of the air just before expansion, and only indirectly upon that of the air as it enters the top of the interchanger. With uniform air supply, the fall of temperature which the air experiences in passing through the interchanger on its way to the expansion valve, depends upon the amount of expanded but unliquefied air which leaves the valve at the temperature of liquefaction, passes upward over the surface

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[1] Bulletin de l'Académie des Sciences de Cracovie, December, 1902. Zeitschrift für komprimirte und flüssige Gase, 7, 10 (1903). Abstract in Chemisches Central-Blatt, 1903, I 543-4.

[2] Bradley and Rowe, p. 337, where it will be noted that "initial temperature" refers uniformly to the temperature of the air which is supplied to the interchanger, and not to that of the same air after it has passed through the interchanger and has reached the expansion valve.

of the interchanger, withdrawing heat therefrom, and finally passes out at the top of the liquefier. If the interchanger presents a sufficiently large surface, the temperature of this outflowing air becomes practically the same as that of the inflowing current. During equilibrium, the quantity of this outflowing current is constant, and is exactly equal to that of the inflowing air less that of the liquid air which accumulates in the reservoir and so is withdrawn from circulation. This being the case, the temperature of the high pressure air just before expansion is constant.

So soon however as the cooling effect of the outflowing current is supplemented by precooling from any external source, the total heat withdrawn from the inflowing current is greater, and its temperature falls accordingly throughout the entire length of the interchanger. In so far, assuming for the sake of simplicity that the specific heat of air is constant for all temperatures, it is clear that the fall in the temperature of the high pressure air at the top of the interchanger, which is due solely to the external precooling, would shortly be matched by an equal fall at the bottom of the interchanger, just above the valve. But it is equally clear that the increased yield of liquid thus secured, leaves a smaller amount of unliquefied air at the service of the interchanger. Thus a withdrawal of heat from the high pressure air outside of the liquefier diminishes to some extent the withdrawal of heat from the same air after it has entered the liquefier, and it comes to pass as was stated above that the full value of external precooling is not realized.

To be sure, the loss incurred from this cause amounts to only a few percent of the total gain from precooling, and is not a very serious matter in its effect on yield. Neither is the further loss which arises from the fact that the outflowing current leaves the liquefier at a lower temperature than before, namely, at the new temperature of the air supply, and consequently carries away *per gram* less heat than before. The fact of such losses does serve, however, to emphasize the

very extraordinary character of the relation between the temperature of the air supply and the yield of liquid air which was brought out by our earlier experiments. If "initial temperature" in those experiments had been taken at the valve instead of at the top of the interchanger, the effect of precooling upon yield would have appeared still greater.

It has been assumed in the foregoing discussion that the surface of the interchanger is sufficient to permit of complete thermal equilibrium between the inflowing and outflowing currents of air. Obviously, an interchanger which is ample when the temperature of the air supply is low, may not be when the temperature is higher. In such a case, precooling would mean, among other things, that a condition of imperfect thermal interchange would be replaced by one of perfect functioning in this respect, and so lead to an increase of yield far in excess of that due to the fall of temperature *per se*.

Now the observed increase in yield in the experiments cited, from 0.74 liter at 92° to 1.94 liters at 30° is in fact partly accounted for in just this way. At 92° the outflow was 5° or 6° colder than the inflow, and of course the yield suffered in consequence. There was still a difference, though much smaller, at 59°. Indeed the balance is never exact, in practice, at any temperature. However, at 30°, and at temperatures still lower, the difference is so very small and so constant that it is quite negligible.

Throwing out the readings above 30° therefore as being certainly influenced by the inadequacy of the interchanger, we note that precooling from 30° to 2° increased the yield from 1.94 to 2.80 liters, or, reckoned on the basis of one horsepower per hour, from 274 to 396 cm^3, a gain of 122 cm^3. Schrötter's formula calls for a gain of only 59 cm^3! In other words, the effect of external precooling is twice as great as it should be on the basis of the Joule-Thomson effect.

Clearly there is urgent need of temperature measurements, taken at the valve, before one can discuss, with satis-

faction, such questions as these. We hope soon to be able to furnish them.[1]

Such extraordinary disparity between the change of initial temperature and the increase of yield which it caused led us at once to the query whether the liquid air itself, as produced by the liquefier, could not be so employed in precooling as to more than replace itself, led us, in short, to experiments on internal precooling.

The most obvious device for the attainment of this object is the insertion into the high pressure circuit, between the bottom of the interchanger and the valve, of a suitable length of pipe so coiled as to be immersed in whatever liquid air may be lying in the reservoir. This device was employed both by Dr. Cottrell[2] and by the writers, with this difference, that in Prof. Cottrell's arrangement the extension, or auxiliary coil, was always entirely immersed in liquid air, and the comparison of yield secured with and without its aid was made possible by the use of two expansion valves, which were used alternately. One of these took air directly from the interchanger, in the usual way, without the use of the auxiliary coil, and so without internal precooling, while the other drew its supply of air from the interchanger indirectly through the auxiliary coil.

In our experiments, on the other hand, but one valve was used. The appendix, as it may be called for brevity's sake, wound in the shape of a cylindrical shell with vertical axis, was so disposed that its lower end was a little higher than the bottom of the liquid air reservoir. Thus, after each drawing of liquid air from the reservoir, fresh liquid could accumulate for a short period—a little less than four minutes, before actual immersion began. If drawings were made at intervals of less than four minutes, therefore, immersion did not occur at all. If they were made at longer intervals, there was immersion of the appendix for a period which increased

[1] Assisted in part by a grant from the Hodgkins Fund of the Smithsonian Institution.

[2] Jour. Phys. Chem., 10, 267 (1906).

with the interval itself. Thus with a ten minute interval, which was about as large as was practicable with regard to the dimensions of the reservoir, there would be about four minutes of accumulation each time without immersion, followed by six minutes with more or less of it. At the end of this interval, about half of the appendix, approximately 140 cm of tubing, lay below the normal level which the liquid would have attained if quiescent, while the upper half was almost entirely covered by the froth of the rapid ebullition.

Figure 1 illustrates this arrangement. AA is the lower end of the interchanger, which is enclosed in the casing GG. C is the appendix, enclosed in the reservoir FF, and communicating with the interchanger and with the valve D by the pipes BB and HH respectively. The liquid air is withdrawn through E.

Obviously if there were any advantage in this method of precooling, it would be made manifest by a comparison of the yields obtained during accumulation periods of different length.

At any rate, there could be no question that notable precooling was both possible and was actually secured by this arrangement.

That there is ample room for such precooling was shown in our former paper,[1] for the temperature of the high pressure air inside the lowest disc of the interchanger cannot be lower than —102°, and beyond any question is considerably higher than that. At the very least, therefore, there is opportunity for from 90° to 100° of precooling before the high pressure air ceases to be able to absorb heat from the outflowing current. Under these circumstances, the formula of Schrötter seems to promise that the amount of liquid consumed in precooling would be much more than made good by the resultant increase in production. The promise was not fulfilled. The rate of accumulation was practically constant, whether the appendix was immersed or not. The liquid air used for precooling was exactly replaced.

[1] Bradley and Hale, p. 391.

Table I gives the yield of liquid air in two runs. In the first, drawings were made at intervals of three, five, six, and ten minutes; in the second, at intervals of four and ten minutes.

The duration of each interval was counted from the beginning of one drawing to the beginning of the next. The number of seconds required for the actual discharge of the liquid was practically the same for all the drawings of the same accumulation period. No records were made, either at the beginning of the runs or after a change in the accumulation period, until equilibrium was fully established, as shown by the concordance of yields obtained.

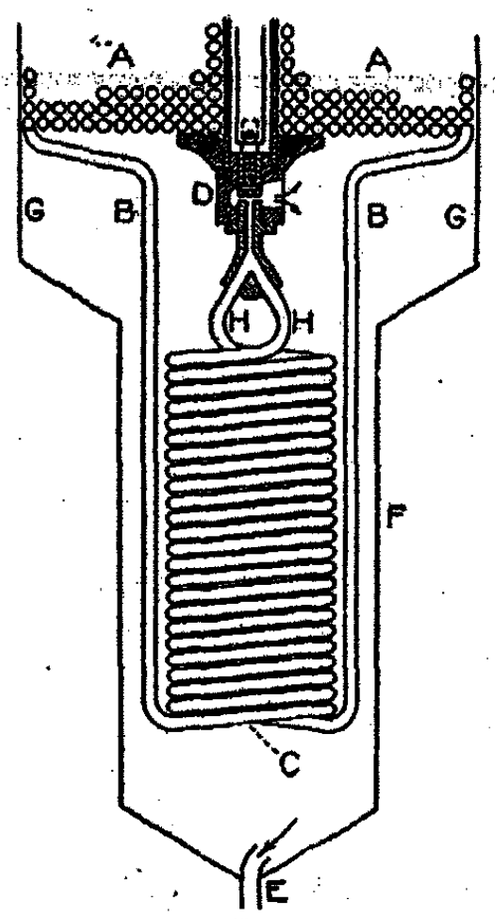


Fig. 1

The table also exhibits the efficiency of the liquefier for the same periods. This is obtained by dividing the weight of liquid air produced by that of the air supplied to the liquefier during the same time. The amount of the air supply was measured at the close of the respective runs in the manner already described.[1]

[1] Bradley and Rowe, p. 332.

TABLE I

	Accumulation period Minutes.	Liquid air cm^3	Liquid air liters per hour	Efficiency of liquefier Percent
A	6	250 255 255 250 275 250 250	2.54	8.75
	10	410 425 420 410 410	2.49	8.58
	5	210 220 210 210	2.55	8.78
	3	125 125 125 125	2.50	8.61
B	4	165 160 160 165 160 165 160	2.43	7.83
	10	410 400 400 415 400	2.43	7.83

The moment when the accumulating liquid in the reservoir begins to envelope the lowest turn of the appendix is

marked by two closely connected phenomena. One of these is a very considerable and very sudden increase in the volume of the air which escapes from the top of the liquefier,[1] and, following this almost immediately, a fall of pressure as indicated on the high pressure gauge of the compressor.

The sudden outrush of air is explained partly by the violent boiling of the liquid air when it comes into contact with the comparatively warm coil. At the same time, however, the high pressure air within the pipe becomes denser through loss of heat, and flows more rapidly through the valve. This makes a heavier demand upon the reserve air in the purifiers, and the pressure of the latter runs down accordingly, unless the expansion valve is at once suitably adjusted. These phenomena always occur at the same moment in the accumulation period, if the liquefier is running steadily, and the new equilibrium which is secured by the adjustment of the valve is not again suddenly disturbed during the period, until the liquid is next withdrawn.

The moment, however, when the level of the liquid during withdrawal falls again below the end of the appendix, a correspondingly sudden decrease in the volume of the exhaust occurs, which has to be checked at once by opening the expansion valve to its former position.

No one who has had the responsibility of adjusting the valve to these sudden changes in the flow of the high pressure air through it, is left in any doubt as to the thoroughness of the precooling which is secured by the immersion of the appendix. Exactly what the initial temperature thus attained is, it is of course impossible to say, in the absence of direct measure-

[1] As the exhaust necessarily meets a certain amount of resistance in the pipe which conducts it back to the compressor, its pressure is slightly above atmospheric. The resistance is constant if the amount of the air is constant. In the usual manner, an arrangement was provided whereby the slight pressure necessary to overcome this resistance was measured by a column of mercury. The latter serves thus as a very sensitive indicator of the amount of air which is returning to the compressor and is incidentally a useful guide for adjusting the expansion valve.

ments. That it was as low at any rate as the critical temperature of air, seems to us extremely likely. The interest which attaches to this point is increased by the recent insistence of Pictet,[1] that high pressure air once cooled to, or below, its critical temperature—which, in other words, has been changed into a liquid—can no longer produce any cooling effect on passing through an expansion valve. Pictet's view will be made clear by the following quotation.[2]

"Indem wir die flüssige Luft sich in dem Reservoir ansammeln liessen, welches eine lange Schlange [the interchanger] abschliesst, die beständig die comprimirte und abgekühlte Luft zuführte, kamen wir dazu, die letzten Windungen mit dieser angesammelten flüssigen Luft zu netzen. Wir haben dabei constatirt, was wir übrigens vorher gesehen hatten, das nämlich die ganze Luft vor der Entspannung sich verflüssigte, der Druck von 80 Atm. auf 60 fiel, dann auf 50, dann auf 40 etc. und die erhaltene flüssige Luft die verdampfte völlig ersetzte, indem sie nur eine schwache Vermehrung zuliess zufolge der Kompressionsarbeit und der Arbeit bei der Entspannung der erhaltenen flüssigen Luft, die von einem hoheren auf atmospherischen Druck übergeht. Diese Maschine hat in dieser Weise drei Tage ohne Unterbrechung funktionirt und lief erte dadurch einen bündigen Beweis fur dieses klassische Theorem, das uns hier beschäftigt, dass nämlich die bei der Entspannung eines Gases nach der Beendigung des molecularen Sturmes erhaltene Abkühlung nur von der äusseren Arbeit der gasförmigen, vor der Entspannung abgekühlten, aber nicht verflüssigten Gasmassen herrührt."

In Pictet's liquefier accumulation practically ceased, for three days of continuous running, from the moment the liquid in the reservoir came into contact with the lower end of the interchanger. In the experiments of Dr. Cottrell and in those

[1] Zeitschrift für komprimirte und flüssige Gase, 7, 1903-4, 22, 23, 37, 52; 8, 1904-5, 13.

[2] Loc. cit., 8, 13.

of the writers, accumulation went on at precisely the same rate as before, from what is constructively the same moment.

There is one apparent way of explaining this flat contradiction. It will be noticed that Pictet makes no mention of any expansion valve at the base of his interchanger. In fact, his statement regarding the fall of pressure which occurred at the moment of immersion seems to indicate that his interchanger ended in an orifice of fixed size. This supposition gains plausibility from the fact that precisely this arrangement was employed in other experiments which are described in the articles referred to. If this is correct, accumulation ceased, not because of precooling, but because the pressure ran down—how far down, he does not say! And the pressure ran down because there was no way of stopping it.

To be sure, Pictet expresses just as decisively the further dictum[1] that the yield of a liquefier whose interchanger has surface enough for perfect functioning, is independent of the pressure, provided the latter is not less than 25–30 atmospheres—or in other words that the only reason why in practice increase of pressure increases the yield is that the interchanger is not large enough for a complete thermal balance.

But we have further shown[2] how profoundly the yield is affected by change of pressure, and that too in a liquefier whose imperfection in the matter of thermal interchange never exceeds 2° for pressures between 1500 and 3000 pounds except indeed where the temperature of the air supply is higher than about 30°, as has already been said. That variations in the functioning of the interchanger, which are represented by less than 2° of difference between the temperature of the inflowing and outflowing currents can account for the fact that a yield of 1.6 liters at 1500 pounds rose to 2.84 liters at 2665 pounds, in other words, that the percentage of liquefaction rose from 4.5 to 8.6, is quite out of the question.

Even when the appendix is not actually immersed in liquid air, it is exposed more or less directly to the drip of

[1] Loc. cit., 7, 40.

[2] Bradley and Rowe, p. 339.

liquid from the expansion valve, and to the fog of liquid droplets which lie above the accumulating liquid. Consequently there is always a certain amount of internal precooling which does not occur when the appendix is absent.

In order to see whether this measure of precooling, which could certainly never be accused of extending to the critical temperature of air, has any effect on the yield, runs were made in which the appendix was alternately present and absent. As the amount of air delivered by the compressor is never quite the same in any two runs, however uniform it may remain during the continuance of either one of them, and as the efficiency of the liquefier varies somewhat with the amount of the air supply, as well as because of certain other circumstances which cannot always be clearly traced, it was desirable to make a considerable number of these runs in order that the comparison should be as decisive as possible. Out of a dozen or more, six are here presented, each of which seems to be entirely normal. In connection with each of the others, some circumstance was noted, during the run itself, whose influence threatened to obscure the main issue involved. In two, for instance, the liquid air ran cloudy, indicating that the purifiers were not functioning properly. The trouble was discovered in the KOH cylinder which needed recharging. In another, a small leak occurred in the inner casing of the liquefier, near the lower end of the interchanger. Though it was not serious, the effect, if any, was to diminish the yield of liquid in that particular run. In one of the runs, a coupling in the high pressure circuit developed a small leak, and in still two others near the close of the runs, a readjustment of conditions in the cylinders of the compressor was revealed by the readings of the three lower gauges. None of these circumstances probably had any considerable effect on the final result, but they tended to some extent at least to mask the issue.

Table II contains the six selected runs. Incidentally one may observe in these how the efficiency of a liquefier

may vary without any assignable reason. In the third and fourth runs especially, the amount of the air supply was a little greater than usual, but the yield was a little below normal. It seems likely that slight differences in the manner of "blowing out" the liquefier, that is, clearing the pipes of the interchanger at the beginning of a run from any moisture left in them from the previous run, may account in part for these variations. Whatever their cause may be, no method has yet been found for avoiding them.

As usual, the records do not begin till the establishment of complete equilibrium in the liquefier. The pressure was 2700 pounds. The runs are numbered in the order in which they were made.

TABLE II

With the appendix			Without the appendix		
No.	Yield per hour	Efficiency Percent	No.	Yield per hour	Efficiency Percent
1	2.50	8.61	2	2.63	8.83
4	2.43	7.83	3	2.56	8.10
5	2.53	8.63	6	2.57	8.53
Averages:	2.49	8.36		2.59	8.49

The presence or absence of the appendix is practically a matter of indifference.

The question having arisen whether there was any advantage to be gained by separating the blast of mingled liquefied and unliquefied air into its constituents by means of some centrifugal device, instead of allowing it to impinge violently against the walls of the reservoir, the following runs were made to test the point. In half of them the naked valve was employed. In the other half, the valve was enclosed within a small cylindrical brass box, from one side of which the blast was delivered through a piece of copper tubing having an internal diameter of 3.2 mm. This tube was about 90 cm in length, and was coiled just below the valve into a close

spiral with vertical axis. Into the outside surface of the turns of the spiral, were drilled minute holes, twenty in number, for the escape of the specifically denser liquid air, and on the inside surface, an equal number of holes having a diameter of 3-3.5 mm, for the escape of the unliquefied air. The outer end of the tube was closed. It will be understood of course that the spiral itself was motionless, and that the centrifugal effect was secured by the spiral motion of the air through it.

TABLE III

Naked valve		Separator	
Yield per hour	Efficiency	Yield per hour	Efficiency
2.77	8.48	2.84	8.79
2.55	8.31	2.63	8.65
Averages: 2.66	8.40	2.74	8.72

The difference is not great, but there appears to be an advantage in the use of the separator amounting to 0.3 percent in efficiency. This is equivalent to a gain of nearly 4 percent in output.

The contents of this paper may be thus summarized:

1. The effect of external precooling upon the yield of liquid air is extraordinary, not only from a practical, but also from a theoretical standpoint, being twice as great as would be expected even by the application of Schrötter's formula.

2. Internal precooling has no appreciable effect on the yield. The liquid air used for this purpose exactly replaces itself.

3. Whether the liquid is used while dripping from the valve, or after it has collected in the bottom of the reservoir is a matter of indifference, although the extent of the precooling secured in these two ways is very different.

4. It is difficult to see how the results obtained by external and by internal precooling can be harmonized with the

view that production of cold at the expansion valve is due to the Joule-Thomson effect. It is for the present at least equally difficult to see how the respective results can be reconciled to each other.

5. When the blast from the valve is conducted through a separator, there seems to be an increase in efficiency amounting to 4 percent of that obtained with the naked valve.

Wesleyan University, Middletown, Conn.,
January 2, 1906

ADSORPTION OF DISSOLVED SUBSTANCES

BY PERCY N. EVANS

The term "adsorption" is here used to mean that action of solids on solutions by which the concentrations of the solutions are altered in immediate proximity to the solid surfaces. Whether the result is due to an attraction between the solid and the solute or is a surface phenomenon of the solution, is uncertain. A review of the principal work already done in this field of inquiry has recently appeared in this journal with a report of original investigations by Lyman J. Briggs.[1]

A number of experiments have been made at various times by the writer, with the assistance of students, and the results have not yet been published except in outline;[2] though the investigation is incomplete it seems best to present without further delay the results so far obtained.

A preliminary series of experiments was carried out, with the assistance of Mr. Donald Davidson, to ascertain how general the adsorption of dissolved substances by solids might be, and the magnitude of the effects. At that time the importance of some factors, such as the relative quantities of adsorber and solution, was not realized and the data were not recorded, so that the experiments cannot be discussed on the same basis as later ones; the following summary will here suffice:

Twentieth-equivalent-normal tartaric acid showed a loss of nearly 12 percent in acidity of the supernatant solution with filter paper; twentieth-normal potassium hydroxide about the same in alkalinity with filter paper; 2.6 percent sucrose solution with animal charcoal was reduced to 1.9 percent, by polarimetric measurement; fiftieth-normal acetic acid with ignited precipitated silica gave a loss in acidity of over 5 percent; fiftieth-normal hydrochloric acid with cotton

[1] Jour. Phys. Chem., 9, 617 (1905).

[2] Proc. Indiana Acad. Sci., 1901.

cloth showed 4 percent loss in acidity; fiftieth-normal hydrochloric acid with ignited silica gave 2.5 percent loss in acidity; fiftieth-normal ammonia with cotton cloth gave about 15 percent loss in alkalinity. All of these experiments showed, then, a positive adsorption of from 2.5 to 27 percent of the dissolved substance.

Several other experiments showed no effect whatever; 2.5 percent sucrose with sugar-charcoal, with lamp-black, with sand; tartaric acid (concentration not recorded) with cotton cloth; tenth-normal sodium thiosulphate solution (reduction equivalent) with ignited precipitated silica.

Some experiments with sodium chloride solutions and filter paper seemed to indicate negative adsorption—a gain in the strength of the supernatant solution—but this result was afterwards found to be due to chlorides in the paper, none of the laboratory supply being entirely free.

The conclusion from this series of experiments is that while adsorption is very pronounced in some cases, it is not shown by all solids with all solutions.

A second series of experiments, made with the assistance of Miss Mary E. Brown, was a more systematic investigation of the behavior of filter paper towards solutions of hydrochloric acid of various strengths.

The procedure followed in each experiment was to place 100 cc of the hydrochloric acid solution in a bottle, add 5 grams of air-dried filter paper cut into small pieces, a piece at a time to insure uniform contact with the solution, stopper the bottle, agitate thoroughly but not violently enough to disintegrate the paper, and finally to titrate 10 cc of the supernatant solution and of the original solution not treated with paper, respectively, with a sodium hydroxide solution of somewhat less than equivalent strength, using phenolphthalein as indicator. Several titrations of each kind were made in every case.

Regarding the time of standing of the solution in contact with the paper, it was found experimentally that the amount

of adsorption in a particular case was identical after various periods ranging from five minutes to a week. It may be remarked that this would seem to exclude the possibility of the change in concentration being due to chemical action. The results obtained were as follows:

HYDROCHLORIC ACID SOLUTIONS AND FILTER PAPER

Gram-equiv. per liter	Liters per gram-equiv.	Percent of solute removed	Milligrams of solute removed per gram of adsorber
1.030	0.97	doubtful	doubtful
0.357	2.80	doubtful	doubtful
0.278	3.60	0.66	1.64
0.166	6.03	1.09	1.32
0.082	12.06	1.28	0.78
0.062	16.20	1.88	0.66
0.043	23.50	2.52	0.68
0.031	32.70	3.07	0.56
0.030	32.80	3.18	0.58
0.023	43.88	4.61	0.64
0.021	48.20	4.85	0.74
0.017	58.24	5.98	0.60
0.014	72.70	8.81	0.72
0.010	96.40	8.12	0.62
0.008	116.38	13.98	0.72
0.007	144.80	14.72	0.62

The figures found for the percent of acid removed form a fairly regular series, increasing with the dilution, but for the highest two concentrations the effect was so slight as to make it doubtful whether any adsorption took place, there being no difference in the solutions treated and those not treated with paper according to most of the titrations.

The absolute weight adsorbed is nearly uniform through a wide range of concentration; that these figures do not form a regular series is to be expected from the experimental nature of the work—the calculation of small differences between comparatively large measured quantities. This is particularly true at the beginning of the series, where the differences

are almost inappreciable, and at the end of the series, where the accuracy of the titrations is less, owing to the difficulty of noting the end-point with highly dilute solutions.

A third series of experiments was made with the assistance of Mr. Edward Mueller.

The first solute chosen was sodium chloride. The procedure was, as before, to place 5 grams of air-dried filter paper in contact with 100 cc of the solution, and to determine the difference in concentrations of the supernatant solution treated and that not treated with paper. In this series chlorine was determined volumetrically with standard silver nitrate, using potassium chromate as indicator, the silver nitrate solution being approximately equivalent in strength to the test solutions in each case. The filter paper was found to contain chlorides, but uniformly distributed, and instead of washing out the chlorine as in earlier work, allowance was made for its presence.

The results obtained were as follows:

SODIUM CHLORIDE SOLUTIONS AND FILTER PAPER

Gram-equiv. per liter	Liters per gram-equiv.	Percent of solute removed	Milligrams of solute removed per gram of adsorber
0.02	50	0.00	0.00
0.01	100	1.36	0.16
0.005	200	2.45	0.14

A series of experiments made in just the same way with potassium chloride solutions gave the following results:

POTASSIUM CHLORIDE SOLUTIONS AND FILTER PAPER

Gram-equiv. per liter	Liters per gram-equiv.	Percent of solute removed	Milligrams of solute removed per gram of adsorber
0.100	10	doubtful	doubtful
0.067	15	0.27	0.27
0.050	20	0.81	0.60
0.033	30	1.18	0.58
0.013	75	2.00	0.39
0.007	150	2.55	0.25
0.005	200	2.75	0.20

Two experiments with barium chloride solutions, carried out in the same way except that chlorine was determined gravimetrically as silver chloride, gave the following results:

BARIUM CHLORIDE SOLUTIONS AND FILTER PAPER

Gram-equiv. per liter	Liters per gram-equiv.	Percent of solute removed	Milligrams of solute removed per gram of adsorption
0.020	50	0.00	0.00
0.005	200	0.00	0.00

The concentrations are here expressed in terms of equivalent-normal.

A series of experiments with hydrochloric acid solutions and filter paper carried out in the usual way gave the following results, the determinations being made volumetrically with standard sodium hydroxide solution and phenolphthalein as indicator:

HYDROCHLORIC ACID SOLUTIONS AND FILTER PAPER
(SECOND SERIES)

Gram-equiv. per liter	Liters per gram-equiv.	Percent of solute removed	Milligrams of solute removed per gram of adsorber
0.50	2	0.00	0.00
0.25	4	0.57	1.04
0.20	5	1.48	2.15
0.10	10	2.49	1.81
0.04	25	4.96	1.44
0.02	50	9.46	1.38
0.01	100	13.03	0.95
0.004	250	23.64	0.69

Comparing this series of experiments and the earlier one with hydrochloric acid and filter paper, it will be noticed that the adsorption percent for corresponding concentrations is larger in every case in the later series, also for the absolute weight of solute adsorbed. This is probably due to a different grade of filter paper having been employed, as the experiments were performed a year later, and a difference in the average coarseness of the fibre would involve a corresponding difference in the adsorption produced, due to greater or less surface in the same weight.

These experiments with solutions of sodium chloride,

potassium chloride, barium chloride, and hydrochloric acid, with filter paper, all show the following: at highest concentrations there is no adsorption; at lower concentrations the percent of solute adsorbed increases with the dilution, except in the case of barium chloride solutions, which showed no adsorption even at the highest dilution; the absolute weight of solute adsorbed is zero at high concentrations, and increases and then decreases with increasing dilution, except barium chloride solutions, which showed no adsorption.

A fourth series of experiments was made, with the assistance of Miss Frances M. DeFrees, on the adsorption of copper sulphate and of potassium chloride from their solutions by filter paper.

In each experiment 100 cc of the solution stood in contact with 5 grams of filter paper, as in the preceding experiments. Copper was determined volumetrically with an approximately equivalent solution of potassium cyanide. Here, again, experiment showed the result to be independent of the time of standing, up to forty-eight hours. The following results were obtained:

COPPER SULPHATE SOLUTIONS AND FILTER PAPER

Gram-equiv. per liter	Liters per gram-equiv.	Percent of solute removed	Milligrams of solute removed per gram of adsorber
1.00	1.0	0.00	0.00
0.50	2.0	0.00	0.00
0.33	3.0	0.00	0.00
0.25	4.0	0.00	0.00
0.20	5.0	0.27	0.87
0.17	6.0	0.85	2.26
0.14	7.0	1.48	3.39
0.10	10.0	2.42	3.88
0.08	12.5	3.18	4.07
0.07	15.0	3.94	4.00
0.05	20.0	4.70	3.77
0.04	25.0	5.57	3.57
0.03	35.0	7.32	3.39
0.02	50.0	9.11	2.91
0.013	75.0	10.42	2.22
0.010	100.0	12.33	1.97
0.008	125.0	15.35	1.96
0.004	250.0	25.77	1.64

Another set of experiments was made with copper sulphate solutions and filter paper, in which the sulphuric acid instead of the copper was determined; this was done volumetrically with standard barium chloride solution, the end-point being reached when no further precipitation resulted on addition of the reagent after allowing the precipitate to settle. The following figures were obtained:

COPPER SULPHATE SOLUTIONS AND FILTER PAPER
(SECOND SERIES)

Gram-equiv. per liter	Liters per gram-equiv.	Percent of solute removed	Milligrams of solute removed per gram of adsorber
0.50	2	0.00	0.00
0.2	5	0.65	2.72
0.10	10	2.91	4.66
0.05	20	4.64	3.71

A comparison of these two sets of experiments with copper sulphate shows as close an agreement as was to be expected in view of the experimental difficulties; the "percent of solute removed" being for half-normal 0.00 in both series, fifth-normal 0.27 and 0.85, for tenth-normal 2.42 and 2.91, and for twentieth-normal 4.70 and 4.64, respectively.

A series of experiments with potassium chloride solutions and filter paper, in which chlorine was determined by titration with standard silver nitrate solutions volumetrically, gave the following results:

POTASSIUM CHLORIDE SOLUTIONS AND FILTER PAPER
(SECOND SERIES)

Gram-equiv. per liter	Liters per gram-equiv.	Percent of solute removed	Milligrams of solute removed per gram of adsorber
0.100	10	0.00	0.00
0.050	20	0.58	0.44
0.029	35	0.69	0.30
0.020	50	1.02	0.31
0.010	100	2.64	0.40
0.004	250	3.91	0.23
0.002	500	5.34	0.16

A comparison of these figures with the earlier series for potassium chloride and filter paper shows a fair agreement throughout.

These experiments with copper sulphate solutions and potassium chloride solutions, show the same points of interest as the earlier ones, namely, at highest concentrations there is no adsorption, at lower concentrations the percent of solute adsorbed increases with the dilution, and the weight of solute adsorbed is zero at high concentrations, increasing and then decreasing with increasing dilution.

A fifth series of experiments was made, with the assistance of Miss Margaret F. Haywood, to compare the behavior of silica with that of filter paper towards solutions of copper sulphate.

The silica was prepared from sodium silicate solution (water glass); hydrochloric acid was added, the material evaporated to dryness, moistened with hydrochloric acid and evaporated to dryness three times, powdered, washed free from chloride, passed through a hundred-mesh sieve, and kept well mixed for use. In each experiment 100 cc of the copper sulphate solution was placed in a bottle with 10 grams of the silica, shaken well, and allowed to settle. The copper sulphate solution, both that treated with silica and the untreated, was titrated with an approximately equivalent potassium cyanide solution in presence of ammonia.

The results obtained were as follows, the concentrations being expressed in terms of equivalent normal strength:

COPPER SULPHATE SOLUTIONS AND SILICA

Gram-equiv. per liter	Liters per gram-equiv.	Percent of solute removed	Milligrams of solute removed per gram of adsorber
1.000	1	0.00	0.00
0.500	2	0.00	0.00
0.250	4	0.00	0.00
0.200	5	doubtful	doubtful
0.100	10	0.00	0.00
0.050	20	doubtful	doubtful
0.033	30	0.00	0.00
0.025	40	0.86	0.17
0.024	42	0.98	0.19
0.022	45	2.48	0.44
0.021	48	3.52	0.59
0.020	50	4.13	0.68
0.017	60	4.92	0.69
0.013	75	5.06	0.53
0.010	100	5.05	0.40

It will be observed that for corresponding concentrations the adsorption is much less marked with silica than with filter paper; this may be due to the difference in the chemical nature of the two materials or to smaller surface in the case of the silica. The results with silica show all the peculiarities already discussed earlier; the dilution at which adsorption first unmistakably appears is much higher with silica than with filter paper—fortieth-normal and fifth-normal. The dilution at which the maximum weight of solute is adsorbed is also much higher with silica than with filter paper—sixtieth-normal and twelfth-normal.

Conclusions

Some solutions show adsorption with filter paper, silica, and other solids, some solutions do not.

Some solutes show adsorption in dilute solution but not in concentrated solution.

No cases were found of negative adsorption.

The proportion of solute removed increases with the dilution.

The weight of solute removed by the adsorber shows with increasing dilution, first an increase then a decrease.

Chemical Laboratory of Purdue University,
Lafayette, Indiana, January, 1906

NEW BOOKS

Outlines of Inorganic Chemistry. *By Frank Austin Gooch and Claude Frederic Walker. 14 × 20; pp. xxiv + 514. New York: The Macmillan Company, 1905. Price: bound, $1.75 net.*

Laboratory Experiments *to Accompany Outlines of Inorganic Chemistry. By Frank Austin Gooch and Claude Frederic Walker. 17 × 21 cm; pp. 104. New York: The Macmillan Company, 1905. Price: paper, $ .50.*—The preface to this work opens with the following statement: "In this new presentation of a plan of study . . . it has been our aim to introduce the student to chemistry by consideration of the simplest and fewest things."

The work is divided into two parts; the first is called "Inductive," and is devoted through its 230 pages mainly to theoretical considerations with just enough information of a concrete kind so that the student may "touch bottom" here and there. The second part, called "Descriptive," gives an account in 490 pages of all the well-established elements; at least there are seventy-eight of them in the index.

In the theoretical part, besides matters customary and familiar in text-books for beginners, one finds, of course, a chapter on Electrical Equivalents and Ions; then there is one on Action and Equilibrium, including eight pages on the Phase Rule; then Heat and Thermal Equivalents; Molecules; Valence; and finally one on Theory, in which loose ends are gathered together, and such matters as the relations of atoms in space, electrons, radio-activity, etc., receive due attention.

With the opening of the second part we have a presentation first of all, of a modified, and not simplified, form of the periodic system of the elements, the only elements hitherto studied except by incidental mention being hydrogen, oxygen, and nitrogen. From this point onwards the materials are arranged by the natural grouping, beginning with hydrogen, then the inert gases of the atmosphere, then the group of the alkali metals, and so on to the end.

With regard to the style of the writing, it must be said that the authors have a strong leaning towards the metaphysical and the exact. There is room for a difference of opinion here, and there is something to be said on both sides of the question as to whether exactness or simplicity should be sacrificed in an elementary text. Any one who will read the first sentence (of 159 words) on page 20, or the definition of an *equivalent* immediately below: "in a compound consisting of two elements the equivalent of an element is the weight of that element which will combine with, replace, or be replaced by either 16 parts by weight of oxygen or that weight of some other element which is capable of combining with, replacing, or being replaced by 16 parts by weight of oxygen," will not be left in doubt as to which side of the contention is sustained by our authors.

The idea of "mass-units," which is used as a transitional idea from equivalents to atoms, offers no obvious simplification in introducing the atomic theory; since the mass-units really are atoms under another, and more cumbrous name. And about the time when the student is becoming accus-

tomed to the term, he is told "the mass-units may be called atoms," and "obviously our system of *symbols* adapted to indicate mass-units and the aggregation of mass-units in molecules may be applied without change to atoms and aggregations of atoms." One is disposed to ask why this was not said earlier.

To the reviewer's mind the worst fault of the book—and in the authors' minds it may be the chief excellence—is in the unlimited use of structural formulae for inorganic compounds. As one turns over the pages of the second part, one has the sensation of looking at a treatise on dye-stuffs, the pages bristle so with bonds. Everything is laid out for the delectation of the beginner, from complete structural formulae for the hydrated chlorides of calcium and aluminium, to that for tartar emetic; the chapter on valence is a maze of such pictures. Does the student learn these? Are they good for him if he does?

Minor errors are not absent; mis-statements, mis-spellings, and even "equally as well as." But it is not on such small matters that the book must stand or fall; it is rather on its adaptation to its purpose. If this purpose is to be a text-book for beginners the adaptation is certainly imperfect if one takes any account of the condition of mind of the average student. How it might answer as an advanced text is another question; it would have completeness in its favor at least. As to the statement from the preface, quoted at the beginning of this notice, it sounds, after a perusal of the contents, a little like a joke.

The set of laboratory exercises designed to accompany the text by the same authors follows the same general lines in the development of the subject. For a mature student who had time enough at his disposal, they would be excellent; but the course is too long for ordinary laboratory conditions unless severely cut down. There are in all over 300 experiments, a great many of which are really two or three under one heading, besides which there are four partial schemes of qualitative separation. There are a great many new experiments, many of them very useful; and some quantitative exercises, neither too numerous nor too difficult.

The book will be very suggestive to those who are interested in the development of a scheme of laboratory instruction. *A. P. Saunders*

Leçons de Chimie, *a l'usage des élèves de mathématiques spéciales. By Henri Gautier and George Charpy. Quatrième édition, entièrement refondue. 16 × 25 cm; 1pp. 522. Paris: Gauthier-Villars, 1905. Price: paper, 10; bound, 13 francs.*—Part I, "Generalities," is a discussion of theoretical matters, pure and simple, or at least pure; it begins with the distinctions between the physical states; then follows a brief outline of crystallography; then a clear and concise account of the difficulties early encountered in fixing values for equivalents and atomic weights, and the gradual progress along this line, due to the study of gases, of isomorphism, and of specific heats. The later sections are given up to the laws of chemical equilibrium—the theorem of Le Chatelier, the Phase Rule, etc.—with a consideration of individual cases, such as calcium carbonate, several hydrated salts, and others; afterwards, reaction velocities; then thermochemistry; and finally a description of the common forms of laboratory apparatus, *e. g.*, for generating, collecting, and washing gases, etc.

The second part deals with the metalloids, including only the principal members of this mis-named group, but giving an excellent account of those

which are considered. Special stress is laid in all cases on the practical side, particularly on the commercial methods of preparation.

Several things strike one about the book. First and foremost, it shares with almost all French treatises, a quality of lucidity in the expression of ideas which is hardly to be found in works in other languages. Along with that, however, it has what one may call the French point of view. Würtz crystallized the expression of it when he uttered his famous phrase, "Chemistry is a French science," and his compatriots seem still to think with him. Not that all the names mentioned in the book are those of Frenchmen, but one perceives a disposition on the part of the authors to ignore a little the work of foreigners, or to put it in small type; and the student who takes his information from this book alone will come to the conclusion that the history of chemistry has been, in the main, made in France.

True to French tradition also, there is no enthusiasm here for the atomistic idea; indeed, one of the excellences of the book, if one regards it purely as collateral reading, is that it has no theoretical bias and no theoretical enthusiasms.

The tone of the work in its earlier chapters is markedly philosophical, and adapted to that kind of abstract thinking in which its special audience is supposed to indulge. Yet the style is so clear that any advanced student could read it without much difficulty.

A notable difference from our own texts appears again in the sparing use of formulae. There are not enough equations in the whole book to supply a single chapter of many of our college texts.

Altogether the work is of such a different type from anything our students come into contact with, that it would be an excellent book to use for reference, in courses on inorganic chemistry to maturer students. Needless to say, college freshmen or sophomores would be quite lost in it. But to the older student it gives another standpoint, and would broaden his sense of the science as a whole.

The volume is admirably printed. *A. P. Saunders*

Les Quantités élémentaires d'Électricité: *Ions, Électrons, Corpuscles. Mémoires réunis et publiés par Henri Abraham et Paul Langevin.* (*Société Francaise de Physique: Collection de Mémoires relatifs a la Physique.*) *16 × 25 cm; pp. xvi + 1144. Paris: Gauthier-Villars, 1905. Price: paper, 35 francs.*— These volumes comprise the second series of the collection of important memoirs relating to physics published by the *Société Francaise de Physique*. The choice of editors has been particularly happy: M. Abraham as *Secrétaire Général* of the Society is naturally familiar with the contemporaneous trend of scientific thought, while M. Langevin has not only made important contributions to the subject himself, but as one of the earlier members of the Cavendish laboratory he has a first-hand familiarity with the history of the important researches which have issued and are still issuing (for the Cambridge laboratory seems to have the anomalous power of sending out hosts of highly energized corpuscles without undergoing disintegration) from that great institution. The endeavor has been made in these two bulky volumes to give a fairly complete reproduction of all the papers of moment. The arrangement is alphabetical

for the list of authors, and chronological for each author. To correct the odd arrangement of subjects inevitable in such a classification, an analytic table of contents precedes the two volumes. The authors believe, with reason, that in this way they have done their utmost to facilitate the accessibility of the papers contained. To bring their work within proper limits, applications, details of apparatus and results, radio-active disintegration products, and purely theoretical inquiries (like those of Larmor) have been omitted. In all, about 150 memoirs appear, often in collaboration with the authors.

In the synopsis, the first part relates to ions, their production and properties; the second part to electrons, where in addition to two divisions similarly headed a third is added, setting forth the peculiarly modern developments of electronic mechanics. It is interesting to glance down the list of names to see with whom each class of researches of a given kind originated. The information given is full and documentary. Naturally, the name of J. J. Thomson is conspicuous; but the activity of the other great contributors like Schuster, Hittorf, Crookes, Rutherford, Lenard, Hertz, Sagnac, Becquerel, Curie, Elster, and Geitel, C. T. R. Wilson, Goldstein, Lorentz, Abraham, and many others, is well brought out in its relation to the development of the subject. Surely it is good to be a member of the French Physical Society, when such admirable publications are among the perquisites! *C. Barus*

Experimental Electrochemistry. *By N. Monroe Hopkins. 16 × 23 cm; pp. viii + 284. New York: D. Van Nostrand Company, 1905. Price, bound, $3.00 net.*—The author has devised a number of interesting experiments in electrochemistry and has written a book around them. He has also described these experiments in detail so that any one else ought to be able to reproduce them. Among the very interesting experiments are: the determination of the direction of the current, p. 12; the Soret phenomenon, p. 29; the separation of ammonia and hydrochloric acid, p. 41; the effect of a magnet on a coil of electrolyte, p. 58; conduction through glass, p. 94; preparation of magnesium, p. 105; determination of anode and cathode temperatures, p. 119; simultaneous preparation of white lead and colored pigments; apparatus for making nitric acid, p. 161; aluminum bronze furnace, p. 176; wire resistance furnaces, pp. 195, 199; series arc furnace, p. 202; preparation of chloroform, p. 212; preparation of carbon bisulphide, p. 213.

From the point of view of lecture and laboratory experiments the book is a remarkable success and belongs in a class by itself. Unfortunately the author has not paid the same attention to the other portions of the book and there are a good many passages which could be changed with profit in the next edition. The student should be told that the electrochemical series, p. 10, varies markedly with the nature of the solution. Richards, Collins and Heimrod did not determine the electrochemical equivalent of silver, p. 81. It is not true to say, p. 87, that in the large commercial electrolytic copper refineries Faraday's law has been tested upon enormous scales by the passage of millions of coulombs and found to hold absolutely. On p. 93 some reference should have been made to Warburg and Ihmori's work on glass. On p. 95 it is stated that dilute salt solutions can be frozen more readily than concentrated ones. This statement makes one wonder whether the author really froze his solutions completely. In

view of the work previously done by Davy and by Faraday, the reviewer is very skeptical as to the appearance of appreciable amounts of sulphur at the anode, p. 105, during the electrolysis of concentrated sulphuric acid. Sulphur appears at the cathode in large quantities but at the anode only through the decomposition of hydrogen sulphide. The student will undoubtedly gather from the text, p. 112, the idea that separations with a rotating anode come under the head of constant voltage separations. On p. 118 oxalic acid is an unfortunate selection for showing the effect of current density, because the size of the cathode has practically no effect. On p. 184 it would have been better to have given a real cut of the aluminum cell instead of the fanciful one that is presented. On p. 202 it seems very improbable that the furnace will work as stated if the drawing is anywhere near accurate. On p. 211 one would like to know what becomes of the acetone when distilling off chloroform. On p. 234 the table shows that silver will precipitate copper from its salts. When speaking of the Jacques cell, p. 256, the author implies that the carbon cannot have been oxidized, because the caustic soda would have then been converted to carbonate. This is exactly what happened and the Jacques cell failed because there was no way of preventing the quantitative deterioration of the fused caustic.

There is one other criticism which must be made about this book. It contains a mass of references to unpublished work by the author. This is a very serious defect. We are given conclusions based on evidence which is not accessible to us and which we are therefore unable to check. So far as one can judge, the experimental work of the author has been very interesting and might have been very valuable. There seems to be no justification for the failure to publish.

With the exception of the last defect, the errors cited above are not serious because most people will recognize them just as they recognize the numerous misprints. They should not blind us to the fact that we have here an exceptionally clever piece of work and that the book is strong in those points in which most text-books on the subject are weak. If the author will publish his data and will revise his text, he will have a book of which he can be proud.

Wilder D. Bancroft

Traité de Physique. *By O. D. Chwolson. Ouvrage traduit sur les Éditions russe et allemande par E. Davaux. Édition revue et considerablement augmentée par l'Auteur, suivie de Notes sur la Physique théorique par E. Cosserat et F. Cosserat.*

Tome premier, premier Fascicule: 16 × 25 cm; pp. xiii + 407. Paris: A. Herman, 1906. Price: 16 francs.

Tome deuxième, premier Fascicule: 16 × 25 cm; pp. vii + 202. Paris: A. Hermann, 1906. Price: 6 francs.—Chwolson's treatise on physics, since it began to appear in a German translation from the Russian, has attracted so much favorable attention that a French version of the work has been undertaken. An account of Chwolson's expository method, and of his arrangement of the subject matter, may be found in notices of the three published volumes of the German edition, in this Journal, 7, 133 and 9, 784. The first two volumes of the French edition are to appear simultaneously in successive parts, and the first part of each of these volumes is now out. The initial section from the

first volume contains the general introduction, together with the chapters on the fundamental principles of mechanics and on physical measurements; and that from the second volume contains the chapters on the emission and absorption of radiant energy, on its velocity of propagation, and on its reflection and refraction. Numerous additions are to incorporate the results of recent researches, and the scope of the work is to be broadened by the inclusion of extensive "notes" on theoretical physics. Two of these notes appear in the first part of the first volume. One is a fine essay by Eugène and François Cosserat, on dynamics; and the other, by the translator, is an elaborate chapter on the theory of integrating machines. The French text is clear and fluent, and the mechanical execution of the volumes is pleasing. *J. E. Trevor*

Chemie der alicyklischen Verbindungen. *By Ossian Aschan. 15 × 23 cm; pp. xlvi + 1163. Braunschweig: Friedrich Vieweg und Sohn, 1905.. Price: paper, 40; bound, 42 marks.*—According to the author's definition, alicylic compounds are the organic substances which contain one or more rings of carbon atoms and resemble in chemical properties the fatty compounds. The group includes the cyclo-paraffins and the compounds formed from them as the result of the elimination of hydrogen. In order to exclude benzene derivatives, only the substances which show chemical properties similar to those of the unsaturated fatty compounds are included.

The book is divided into two parts: The first, consisting of 388 pages, gives an account of the historical development of the chemistry of the group, and discusses, at some length, the influence of the ring-structure on the physical and chemical properties of the members of the group. The historical account includes a summary of the work on the hydration of benzene and naphthalene and their derivatives, the syntheses of Freund, Perkin, Jr., Zincke, and Hantzsch, the tension theory of Baeyer, the preparation of ring-compounds by means of diazoacetic ether and diazo-methane, and the work on the terpenes and camphor.

In the second part of the book a systematic account is first given of the general methods of preparation of the various classes of compounds, such as saturated and unsaturated hydrocarbons, halogen derivatives, acids, amines, etc. Then follow detailed descriptions of nearly five thousand compounds.

The author's work appears to have been well done. The parts of the book which have been carefully read by the reviewer have been found to treat the subject adequately. The logical manner in which the great mass of facts has been arranged is worthy of praise. The book contains a description of the work which has appeared in the field of the chemistry of the alicyclic compounds up to the time of its publication, 1904–1905. It will prove of great value to workers in this field, and to those chemists who desire to broaden their knowledge of the compounds discussed, which have taken an important place in general organic chemistry within the last few years. *James F. Norris*

Baumert's Lehrbuch der gerichtlichen Chemie. *Zweiter Band. By M. Dennstedt and F. Voigtländer. 16 × 24 cm; pp. x + 248. Braunschweig: Friedrich Vieweg und Sohn, 1906. Price: paper, 9 marks.*—This second volume deals with the detection of forgeries, the recognition of blood-stains,

etc. In itself this is a specialized branch of chemistry, but the methods described are largely photographic ones and the details of these will interest many chemists outside of those who appear as experts before a jury.

Wilder D. Bancroft

Ueber die Oxydation des Stickstoffes in der Hochspannungsflamme. *By Johannes Brode. 16 × 24 cm; pp. 63. Halle: Wilhelm Knapp, 1905. Price: paper, 2.50 marks.*—The author gives a general account of the work that has been done in making nitric acid from atmospheric nitrogen and then describes in detail his own work with Nernst glowers, platinum and iridium as electrodes. The results are not summed up in a satisfactory manner, but the author does not claim to get as good results as those obtained by Birkeland and Eyde.

Wilder D. Bancroft

Annuaire pour l'An 1906. *Publié par le Bureau des Longitudes. 10 × 15 cm. Paris: Gauthier-Villars. Price: paper, 150 francs.*—We record the appearance of the current issue of this tabulation of astronomical, physical, and chemical data. A new feature is a table of the compositions of a large number of alloys employed in the arts. The special features of the issue are three essays on the solar eclipse of 1905.

J. E. Trevor

REVIEWS

The object of this department of the Journal is to issue, as promptly as possible, critical digests of all Journal articles that bear upon any phase of Physical Chemistry.

General

The atomic weight of silicon. II. *J. Meyer. Zeit. anorg. Chem.*, 47, 45 (*1905*).—Jordis has claimed that the author's silica probably contained a chlorine compound. Experiments have shown that silicic acid, dried at 150°, does not lose all the hydrochloric acid or all the water, but there is no evidence of the formation of a compound. The author's silica was ignited for over five hours at about 1100° and was free from chlorine. Taking Cl as 35.45, the atomic weight of silicon is 28.21. If we adopt, as the author does, the value of 35.470 for chlorine, found by Richards and Wells, the atomic weight of silicon is 28.250. *W. D. B.*

The atomic weights of carbon and beryllium. *C. L. Parsons. Jour. Am. Chem. Soc.*, 27, *1204; Zeit. anorg. Chem.*, 46, *215* (*1905*).—The author has acted on Clarke's suggestion and has taken his results for beryllium acetylacetonate and for basic beryllium acetate as giving him two equations with two unknown quantities, beryllium and carbon. On solving for these he obtains 12.007 for carbon and 9.112 for beryllium. *W. D. B.*

A revision of the atomic weight of iodine. *G. P. Baxter. Zeit. anorg. Chem.*, 46, *36* (*1905*).—Reviewed (9, 595) from Jour. Am. Chem. Soc., 27, 876 (1905).

A revision of the atomic weights of sodium and chlorine. *T. W. Richards and R. C. Wells. Zeit. anorg. Chem.*, 47, *56* (*1905*).—Reviewed (9, 510) from Jour. Am. Chem. Soc., 27, 459 (1905).

Atomic weight determinations of rare earths. *O. Brill. Zeit. anorg. Chem.*, 47, *465* (*1905*).—Using Nernst's micro-balance the author has determined the temperatures at which the excess sulphuric acid can be driven off from several rare earth sulphates; the temperatures at which the basic sulphates form; and the temperatures at which the basic sulphates break down. The temperatures at which the excess of sulphuric acid can be driven off without breaking down the neutral sulphates is about 450°–500°, much higher than that given by Krüss. The author recommends the use of the micro-balance when determining atomic weights of rare earths. *W. D. B.*

The conception of valence. *J. Billitzer. Zeit. anorg. Chem.*, 45, *81* (*1905*).—A reply to Abegg and Hinrichsen (9, 424). The author makes a distinction between total affinity and valence affinity. "The total affinity is the sum of all the valence affinities, but the changes of the single valence affinities are by

no means the same as those of the total affinity. In fact it is quite conceivable that one or more valence affinities might decrease or disappear, while the total affinity actually increases." If one really grasps the full inwardness of this, it is probable that everything else would seem elementary. *W. D. B.*

A constant temperature bath for low temperature. *A. Given. Jour. Am. Chem. Soc.*, 27, 1519 (1905).—A description of a bath to be kept at 15°. The bath is heated by a burner and cooled by means of iced water. *W. D. B.*

One-Component Systems

Amorphous sulphur. *III. A. Smith and W. B. Holmes. Jour. Am. Chem. Soc.*, 27, 979 (1905).—This paper contains the details of the work on the conditions affecting the existence of amorphous sulphur at ordinary temperatures. The main result has already been announced (9, 595) that ammonia increases the rate of change while iodine and SO_2 retard it. *W. D. B.*

The density of chlorine. *F. P. Treadwell and W. A. K. Christie. Zeit. anorg. Chem.*, 47, 446 (1905).—The authors find a density of 2.488 for chlorine at 20° under 730 mm pressure, and a value of 2.489 at 10° under 725 mm pressure, while Moissan and Binet du Jassoneix found 2.490 at 0° under 760 mm pressure. From these data the molecular volume of chlorine becomes 22.0392 liters at 20°, 22.0300 liters at 10°, and 22.0216 liters at 0° when the atomic weight of chlorine is taken as 35.45. There seem to be more decimal places than are warranted by the accuracy of the observations. *W. D. B.*

The application of the van der Waals equation to solids. *C. Benedicks. Zeit. anorg. Chem.*, 47, 455 (1905).—The author criticizes Traube's view (8, 583) that the van der Waals equation has been shown to hold for solids. While admitting that Traube has brought out some interesting relations, the author shows that the van der Waals equation is only one out of many from which the same conclusions might be drawn. The author might also have made the point that the van der Waals equation does not hold for gases or liquids with any degree of accuracy and consequently it is extremely improbable that it holds for solids. *W. D. B.*

Variability of specific gravity. *G. W. A. Kahlbaum and E. Sturm. Zeit. anorg. Chem.*, 46, 217 (1905).—It is proved that twisted, pressed, or hard-drawn wires show a decrease in density, which disappears more or less completely on heating. The wire becomes apparently amorphous and the change to normal conditions has been found by Spring to be accompanied by an evolution of heat. It seems quite possible that under stress the metal transforms itself into that modification which flows the more readily, namely the liquid. This is confirmed by a statement that the density of bismuth increases on drawing. This observation has been questioned by others. *W. D. B.*

The hardness of hammered tantalum. *W. v. Bolton. Zeit. Elektrochemie*, 11, 503 (1905).—Hammered tantalum, containing some oxide, is as hard as the most carefully hardened steel and is very much more ductile. The fact that it cannot be bored by a diamond does not prove that it is as hard as a diamond, though this had previously been assumed. *W. D. B.*

Two-Component Systems

The system, bromine and iodine. *P. C. E. Meerum Terwogt. Zeit. anorg. Chem.*, 47, *203* (*1905*).—The freezing-point curve shows the existence of a solid phase varying continuously from pure iodine to pure bromine. At the composition IBr, the coexisting liquid and solid phases have the same composition. The author is bothered by this because there is neither a maximum nor a minimum in the freezing-point. This is not necessary, as the Gibbs equations show that liquid and solid *must* have the same composition when the freezing-point curve passes through a maximum or minimum and *may* have the same composition when the freezing-point curve has a point of inflection. The vapor composition relations point to the existence in the vapor of the compound IBr. *W.D. B.*

Freezing-, boiling-, and dew-curves for some binary systems. *J. v. Narbutt. Zeit. phys. Chem.*, 53, *697* (*1905*).—The author has studied the behavior of the three bromnitrobenzenes taken two at a time, and also the freezing-curve for diphenylamine and phenanthrene. There are no compounds and no solid solutions. There are neither maxima nor minima in the boiling-point curves and the composition of the vapor differs but little from that of the liquid with which it is in equilibrium. *W. D. B.*

Iodic acid. *E. Groschuff. Zeit. anorg. Chem.*, 47, *331* (*1905*).—Iodic acid does not crystallize with water. The freezing-point diagram shows the existence of ice, HIO_3, $HIO_3.IO_3$, and I_2O_5 as solid phases. The quadruple points are at —14°, +110°, and between 190° and 200°. Conductivity and molecular weight determinations were also made. *W. D. B.*

Barium oxide and its hydrates. *O. Bauer. Zeit. anorg. Chem.*, 47, *401* (*1905*).—$BaO_2H_2.8H_2O$ melts at 78°, the solution boils at 103°. At 109° a new hydrate separates and the boiling-point is said to fall. This last is evidently an experimental error. The new hydrate has the composition $BaO_2H_2.3H_2O$, but the author does not determine either of the quadruple points which limit its existence. The lower quadruple point must be below 78°. *W. D. B.*

Equilibria between solid and liquid phases in ternary, pseudobinary systems. *H. W. Bakhuis Roozeboom and A. H. W. Aten. Zeit. phys. Chem.*, 53, *449* (*1905*).—When a solid melts to a mixture of two liquid forms, the authors propose to call the system a pseudo one-component one. This is a most unfortunate decision and should be reversed at once. While the system in question will behave sometimes like a one-component system and sometimes like a two-component system, its true classification is determined by the true equilibrium. Sulphur is a one-component system though it might be called pseudo-binary when the freezing-point is lowered by the presence of the other liquid form. Under the definition and practice of the authors a salt which forms a hydrate in solution forms a ternary system with water even though it may never behave in any way like a ternary system. If we take into account the polymerization of water we shall call it a quaternary system and that without taking into account the electrolytic dissociation. On this basis we shall never know where any system belongs and all will be unnecessary confusion. The only proper

way, as has been said, is to classify systems according to the true, reversible equilibria and to keep the word "pseudo" for apparent equilibria.

The authors give a systematic presentation of the behavior of systems with a varying apparent number of components. Of special interest is the portion dealing with 'abnormal' solubility curves. *W. D. B.*

Equilibrium in the system, bismuth and sulphur. *A. H. W. Aten. Zeit. anorg. Chem.*, 47, *386* (*1905*).—The author has repeated Pélabon's experiments (8, 364) on the freezing-points of mixtures of bismuth and sulphur. Up to 50 atomic percents of sulphur the two curves are similar, though Aten's data are uniformly higher than those of Pélabon. Aten finds no signs of a maximum near 60 atomic percents of sulphur and his experiments disprove the existence of the phase BiS which Pélabon assumed to exist. Over the range covered by the experiments, Bi_2S_3 appears to be the only compound which crystallizes from the melt. *W. D. B.*

The solubility of phosphorus in ether and benzene. *A. C. Christomanos. Zeit. anorg. Chem.*, 45, *132* (*1905*).—The alleged solubilities of phosphorus in benzene are given from 0° to 80° and in ether from 0° to 35°. It is not explained how the author kept the phosphorus from melting when in contact with hot benzene and there is nothing to show at what temperature the phosphorus did melt. Under the circumstances, the accuracy of the measurements is certainly not great. *W. D. B.*

The basic properties of oxygen. *D. McIntosh. Jour. Am. Chem. Soc.*, 27, *1013* (*1905*).—At low temperatures ether and acetone form crystalline compounds with nitric acid and with chlorsulphonic acid. Ethyl alcohol forms a crystalline compound with nitric acid, but none of the three organic liquids gave a crystalline compound with anhydrous sulphuric acid. The experiments of Cohen and Gatecliff on the interaction of ether and nitric acid are in error. *W. D. B.*

Tantalum and hydrogen. *M. v. Pirani. Zeit. Elektrochemie*, 11, *555* (*1905*).—Tantalum absorbs small amounts of hydrogen, becoming crystalline and brittle. The electrical conductivity also changes. The last traces of hydrogen can only be driven off by heating practically to melting. The author decides that tantalum forms a compound with hydrogen, but it is difficult to see how he reached this conclusion in the face of the evidence. *W. D. B.*

Liquid mixtures of minimum boiling-point. *C. D. Holley and J. T. Weaver. Jour. Am. Chem. Soc.*, 27, *1049* (*1905*).—Mixtures with minimum boiling-point were obtained with propyl bromide and propyl alcohol, ethyl alcohol or methyl alcohol; with isobutyl bromide and the same three alcohols; with amyl bromide and amyl, isobutyl, propyl or ethyl alcohol; with methyl iodide and methyl alcohol; with butyric acid and bromoform; with propyl alcohol and carbon tetrachloride. In a number of other cases considerable additions of one liquid caused practically no change in the boiling points. The results are shown graphically and the data are unfortunately not given. *W. D. B.*

The molecular weight of mercuric iodide. *W. Herz and M. Knoch. Zeit. anorg. Chem.*, 46, *460* (*1905*).—A molecular weight determination for mercuric

iodide in alcohol gave 428 for a finite concentration instead of 453.9. Mercuric iodide is therefore monomolecular and undissociated in alcohol solution. It is rather a pity that two or more measurements should not have been made, so that one could know which way the apparent molecular weight varied with varying concentration. *W. D. B.*

A modification of the Beckman boiling-point apparatus. *G. Rupp. Zeit. phys. Chem.*, **53**, *693* (*1905*).—In the vapor heating apparatus, the inside tube is ground in and can be lifted out to be weighed. *W. D. B.*

The sulphuric acid contact process. *R. Lucas. Zeit. Elektrochemie*, 11, *457* (*1905*).—Having some platinum which was free from iridium the author has repeated the measurements of Bodländer and Köppen (8, 68). The variations in the equilibrium constant are not greater than the probable error. The author takes 18840 cal as the most probable value of the heat of reaction. *W. D. B.*

Multi-Component Systems

The acid iodates of potassium, sodium and ammonium. *P. A. Meerburg. Zeit. anorg. Chem.*, 45, *324* (*1905*).—The author has determined isotherms at 30° for the systems: KIO_3, HIO_3 and H_2O; $NaIO_3$, HIO_3 and H_2O; NH_4IO_3, HIO_3 and H_2O. The solid phases are KIO_3, $KIO_3.HIO_3$, $KIO_3.2HIO_3$ and HIO_3 in the first system; $(NaIO_3)_2.3H_2O$, $NaIO_3$, $NaIO_3.2HIO_3$, HIO_3 in the second system; NH_4IO_3, NH_4IO_3, $NH_4IO_3.2HIO_3$, and HIO_3 in the third. The author claims that a pyro-salt, $Na_2O.I_2O_5$ crystallizes from certain solutions but he gives no reason for calling it this rather than sodium iodate, $NaIO_3$. *W. D. B.*

The phosphates of calcium. *F. K. Cameron, A. Seidell and J. M. Bell. Jour. Am. Chem. Soc.*, 27, *1503*, *1512* (*1905*).—Solubility determinations have been made at 25° for the system, lime, phosphoric acid, and water. The solid phases are monocalcium phosphate, $CaH_4(PO_4)_2.H_2O$, dicalcium phosphate, $CaHPO_4.H_2O$, and a series of solid solutions. The upper limit of the solid solutions does not differ appreciably from dicalcium phosphate. Both the compounds are decomposed by water. *W. D. B.*

The formation of oceanic salt deposits. *J. H. van't Hoff. Zeit. anorg. Chem.*, 47, *244* (*1905*).—The paper deals with the lime salts in the Stassfurt deposits. It is divided into four sections: direct determination of the fields for gypsum, syngenite, glauberite, tachhydrite, and calcium chloride at 25°; indirect determination of the fields for anhydrite, pentasulphate, polyhalite and krugite at 25°; effect of temperature; applications. *W. D. B.*

The phase rule and conceptions of igneous magmas—their bearing on ore deposition. *T. T. Read. Economic Geology*, 1, *101* (*1905*).—The author is considerably amazed that so few writers have applied the theory of the phase rule to rock magmas, and undertakes to show how very simple the application is. He assumes that the components of ordinary rocks may be considered as four, grouping the oxides of lime, magnesia and iron as one, the oxides of alkalies as a second, Al_2O_3 and SiO_2 as the others. He assumes that Fe_2O_3 can replace Al_2O_3 without altering the complexity of the system, and excludes water from consideration. He then deduces that a rock in which four solid phases are

present is stable, and one in which more than four phases appear is unstable. One of the phases which go to form a stable rock is glass. If the author's assumptions were correct, his deductions would be only partly correct; as his principal assumptions are wrong, the deductions are worthless. In illustrating his subject, the author discusses the copper-tin alloys, of which he seems to have a quite extraordinary conception.

To explain the difference in the nature of lavas ejected from a common source, the author drags in the conception of two liquid layers, even quoting the instance of chloroform, acetic acid and water to illustrate the point. He then feels called upon to explain how diffusion might occur in the original magma to separate it into these two layers, and seems to conceive a state in which he has three layers instead of two. It is the experience of both scientists and technical men that the silicates are miscible in all proportions, and it seems rather unfortunate to propose an explanation for which we have no positive facts, and against which we have a very great number. The author mentions the subject of viscosity of magmas, and is as badly lost there as in other parts of the subject. By a 'strict' definition of stability, the author understands that the changes which have taken place are reversible. The subject of ore deposition is practically not discussed at all, although the title might lead one to hope for some new light on the subject.

This paper is quite unfortunate in that the author has undertaken to set before petrographers certain rules whereby they may understand the condition of rocks, which rules are very misleading. It is to be regretted that the author did not make himself acquainted with the subject before undertaking to explain it to others, and one cannot help feeling that as he gets better acquainted with the phase rule, he will be less astonished that so few people have chosen to apply it to igneous rocks. It seems that physical chemistry is sadly in need of some one to save it from its friends. *E. S. S.*

Solubility in mixed solvents. II. *W. Herz and M. Knoch. Zeit. anorg. Chem.*, 45, *262* (*1905*).—The authors have determined the solubility at 25° of potassium bromide, ammonium chloride, and sulphur in mixtures of acetone and water; of mercuric iodides in mixtures of alcohol and water; and of succinic acid, boric acid, and iodine in mixtures of glycerol and water. In no case did Bodländer's formula hold, but the authors console themselves by thinking that the trouble may be due to their own experimental error. *W. D. B.*

Solubility in mixed solvents. III. *W. Herz and M. Knoch. Zeit. anorg. Chem.*, 46, *193* (*1905*).—The authors find that Bodländer's equation $W/\sqrt[3]{S} = const.$ does not hold in general when W is the amount of water, S the amount of salt in a given volume, the remainder of the solution being made up of a liquid A in which the salt is not soluble. The authors propose substituting an equation

$$\frac{(S+A)W}{S+A+W} = const.$$

Their own experiments show that the relation is not accurate so they hope to find a theoretical justification for it. *W. D. B.*

Hydrolysis in non-aqueous solutions. *G. Bruni and A. Manuelli. Zeit. Elektrochemie*, 11, *554* (*1905*).—If fused antimony trichloride be added to half

its volume of formamide, the resulting solution remains clear. If however the antimony trichloride is added to an excess of formamide, there is a precipitate which appears to be a mixture of the compounds $SbCl(NHCOCH_3)_2$ and $Sb(NHCOCH_3)_3$. *W. D. B.*

Equilibria between hydriodic and iodic acids, also between hydrobromic and bromic acids. *V. Sammet. Zeit. phys. Chem.*, 53, 641 (1905).—While the direct equilibrium between hydriodic and iodic acids cannot be measured directly, this can be done if the iodine concentration is kept very low by addition of a silver salt (9, 716). The equilibrium relation can be represented by the equation

$$5H^{\cdot} + 5I' + H^{\cdot} + IO_3' \rightleftarrows 3I_2 + 3H_2O.$$

This shows that the reaction does take place just as one would expect it to, and makes it very probable that the usual explanation for the reaction velocity experiments is the true one, that the reaction proceeds in stages. Bromic and hydrobromic acids give similar results. The equilibrium constants were determined electrometrically as well as analytically. *W. D. B.*

Complex compounds of carbon dioxide with heavy metals. *R. Luther and B. Krsnjavi. Zeit. anorg. Chem.*, 46, 170 (1905).—Ferric and cupric hydroxides are readily soluble in potassium bicarbonate solutions. The heavy metals diffuse through parchment paper and are therefore not present as colloids. Migration experiments showed that these metals formed part of the anion, while electromotive force measurements with copper lead to the view that the complex anion is $Cu(CO_3)_2$." *W. D. B.*

The action of nitrogen on water vapor at high temperatures. *O. F. Tower. Jour. Am. Chem. Soc.*, 27, 1209 (1905).—At 2000° C we have the reactions

$$N_2 + O_2 \rightleftarrows 2NO$$

and

$$2H_2O \rightleftarrows 2H_2 + O_2$$

taking place to a measurable extent. The sum of these two reactions gives

$$N_2 + 2H_2O = 2NO + 2H_2,$$

which shows that nitrogen must react on water vapor at high temperatures to a certain extent. With an iridium tube at 2000° it was shown that this reaction did take place. A satisfactory equilibrium was not reached on account of the low reaction velocity and the diffusion of hydrogen through the iridium tube. *W. D. B.*

Reactions in liquid ammonia. *E. C. Franklin. Zeit. anorg. Chem.*, 46, 1 (1905).—Reviewed (9, 606) from Jour. Am. Chem. Soc., 27, 810 (1905).

The plasticity of clays. *F. F. Grout. Jour. Am. Chem. Soc.*, 27, 1037 (1905).—Plasticity is defined as the property developed in a clay by water, by virtue of which it can be moulded, without crumbling, into forms which remain stiff and unchanged after the removal of the moulding force.

"Sand injures plasticity little at first because the grains are suspended in a plastic mass. It is only when grains are abundant enough to come into contact with their neighbors, that the effect becomes serious, and then both strength and amount of possible flow are injured.

"Certain rare organic colloids increase the plasticity by rendering the water viscous.

"Fineness also tends to increase plasticity.

"Plane surfaces (plates) increase the amount of possible flow. They also give a chance for lubrication by thinner films, thus increasing the friction of film and the strength of the whole mass. The action of plates is thus twofold; but fineness may be carried to such an extent as to break up plate-like grains into angular fragments. The beneficial effects of plates are also increased by the fact that each is so closely surrounded by others in the mass.

"Molecular attraction is twofold in increasing plasticity. As the attraction increases, the coherence and strength of the mass increase, and the amount of possible deformation before crumbling also increases. Fineness increases the action by requiring more water. Colloids and crystalloids in solution may also increase the attraction. It is thus seen to be more active than any other single factor." *W. D. B.*

Metastannic and metazirconic acid. *J. M. van Bemmelen. Zeit. anorg. Chem.*, 45, 83 (*1905*).—The author disagrees with Ruer (9, 431) and gives his reasons for believing that metastannic and metazirconic acids behave similarly. *W. D. B.*

Colloidal silver. *A. Gutbier and G. Hofmeier. Zeit. anorg. Chem.*, 45, 77 (*1905*).—Solutions of silver nitrate and gum arabic in water were treated with hydrazine hydroxide. The precipitates from the more concentrated solutions were olive-green by reflected light, changing to gray in the more dilute solutions. *W. D. B.*

Velocities

A new, very sensitive catalysis by hydrogen as ion. *G. Bredig and W. Fraenkel. Zeit. Elektrochemie*, 11, 525 (*1905*).—In presence of hydrogen as ion, diazo ethyl acetate reacts violently with water. The reaction is a monomolecular one and can be followed by measuring the nitrogen evolved. The reaction can be used for determining concentrations of hydrogen as ion of the general order of $n/1000$ and less. *W. D. B.*

Saponification of esters in heterogeneous systems. *H. Goldschmidt. Zeit. Elektrochemie*, 11, 430 (*1905*).—The author disputes Kremann's view that the apparent rate of saponification of esters in heterogeneous systems depends primarily on the rate of solution of the ester and only secondarily on the reaction velocity of the chemical reaction. This would be true only in case the rate of solution were very low in comparison with the rate of the chemical reaction. In the case under consideration, exactly the reverse is true and we can treat the concentration of the ester in the aqueous solution as constant. This of course is true only in so far as the reaction products cause no change in the solubility. *W. D. B.*

Saponification of esters in heterogeneous systems. *R. Kremann. Zeit. Elektrochemie*, 11, 549 (*1905*).—A rather unsuccessful answer to Goldschmidt (preceding review). *W. D. B.*

Physical chemical studies on zinc alloyed with lead and cadmium. *F. Novak. Zeit. anorg. Chem.*, 47, *421* (*1905*).—The author speaks of zinc and lead as forming solid solutions, which is incorrect. He finds that lead up to 2 percent has no effect on the rate at which zinc dissolves in dilute acids, but that more lead does affect the rate. This must be due either to experimental error or to bad casting. This latter is the more probable since the author states that the metal had to be remelted several times to get good results, which is absurd. The presence of cadmium in rolled zinc containing lead decreases the rate of reaction with dilute hydrochloric acid and increases the rate with dilute nitric acid. This difference is believed to be due to the absence of an 'excess voltage' in nitric acid solutions. *W. D. B.*

Determining chemical equilibria from explosion processes. II. *W. Nernst. Zeit. anorg. Chem.*, 45, *126* (*1905*).—The author discusses a hypothetical case in which the reaction velocity at the moment of explosion is not sufficient to cause the system to reach equilibrium. Formulas are deduced and it is stated that the reaction between nitrogen and oxygen probably comes under this head. *W. D. B.*

Determining chemical equilibria from explosion processes. I. *K. Finckh. Zeit. anorg. Chem.*, 45, *116* (*1905*).—The evidence in regard to the explosion of carbon dioxide and hydrogen is not sufficient to warrant the conclusion that equilibrium is reached at the moment of explosion and that it is not displaced as the gases cool. The evidence is against such a view in regard to the formation of hydrogen peroxide by the combustion of hydrogen and oxygen and in regard to the reaction between nitrogen and oxygen. *W. D. B.*

Effect of temperature on the rate of development of animal life. *R. Abegg. Zeit. Elektrochemie*, 11, *528* (*1905*).—The rate, at which the eggs of sea-urchins develop, a little more than doubles for a temperature rise of 10°. *W. D. B.*

Electromotive Forces

Fundamentals of a general theory of electrolytic solution pressures. *C. Fredenhagen. Zeit. Elektrochemie*, 11, *496* (*1905*).—It is pointed out very properly that "electrically-charged ions" is purely a figure of speech. The author believes that the electrochemical phenomena are fundamental and are not to be referred back to anything else. Galvanic electricity is merely a regulated binary development of chemical energy. We are then introduced to molecular forces and the rest of the paper lacks definiteness, seeming to consist chiefly of a substitution of phrases for facts. *W. D. B.*

Electro-affinity of anions. I. *H. Schafer and R. Abegg. Zeit. anorg. Chem.*, 45, *293* (*1905*).—The authors have studied the solubility relations and tendency to form complexes of a large number of oxalates. The material is classed under four heads: qualitative review of the oxalates with reference to solubility relations and the formation of complexes; the copper oxalate complexes; the silver oxalate complexes; the iron oxalate complexes. The anions are believed to be $Cu(C_2O_4)''_2$, $Fe(C_2O_4)_2''$, and $Fe(C_2O_4)_3'''$ while silver does not enter into an oxalate anion to any great extent. The salt $Fe_2(C_2O_4)_3$ is really ferric ferri-oxalate and not ferric oxalate. *W. D. B.*

Electrolysis and Electrolytic Dissociation

Electrolytic calcium. *J. H. Goodwin. Jour. Am. Chem. Soc.*, 27, *1403* (*1905*).—Metallic calcium was made by the Rathenau process. An Acheson graphite crucible was used and a current of 250 amperes. The calcium was 98 percent pure. The specific resistance at 0° is 3.43 microhms per centimeter cube. (For wires of equal length and diameter it is fifth in the list of conductivity, those ahead of it being silver, copper, gold, aluminum.) For wires of equal weight and length, calcium stands second, the order being sodium, calcium, potassium, aluminum, magnesium, copper, silver, gold, etc. *W. D. B.*

Some observations on the deposition of alloys from mixed solutions. *C. B. Jacobs. Jour. Am. Chem. Soc.*, 27, *972* (*1905*).—The author uses a slowly rotating cathode and two anodes of different metals connected with different generators. By connecting a zinc anode to a high voltage generator and a nickel anode to a low voltage generator, a satisfactory deposit of a zinc-nickel alloy was obtained. With zinc and copper in a sulphate solution brass was precipitated. Since the apparatus cannot possibly work as stated, it must be that the author has overlooked something in his description. From the cut we see that one anode is on one side of the cathode and the other on the other. It seems probable that the solutions on the two sides of the cathode are not the same and that the author is precipitating zinc on one side of the cathode and copper on the other. If this is true, the alleged alloy is merely a series of concentric films of each metal alternately. If this is not the case, the result calls for explanation. The author's view of the process cannot be right. *W. D. B.*

The use of the rotating anode and mercury cathode in electro-analysis. *L. G. Kollock and E. F. Smith. Jour. Am. Chem. Soc.*, 27, *1255* (*1905*).—The authors have studied the deposition of zinc, copper, nickel, cobalt, chromium, and iron, using a rotating anode and a mercury cathode. Up to 0.4 g can be precipitated quantitatively in ten to twenty-five minutes. Very valuable time-precipitation curves are given. *W. D. B.*

The use of the rotating anode and mercury cathode in electro-analysis. *L. G. Kollock and E. F. Smith. Jour. Am. Chem. Soc.*, 27, *1527* (*1905*).—Using a rotating anode and a mercury cathode it is a simple matter to precipitate quantitatively 0.95 g Cd in 10–15 minutes, 0.41 g Sn in 7–10 minutes, 0.37 g Ag in 4–5 minutes, 0.36 g Hg in 3–4 minutes, 0.23 g Bi in 12–15 minutes. It was not found possible to make large amounts of silver halide adhere well to a rotating silver anode. If one only wishes to determine the metal in a halide solution, the bad effect of the halogen can be eliminated by adding toluene. A number of experiments are cited to prove this. *W. D. B.*

The electrolytic determination of mercury with a rotating anode. *R. O. Smith. Jour. Am. Chem. Soc.*, 27, *1270* (*1905*).—Mercury can be precipitated satisfactorily from a nitrate or from an alkaline sulphide solution. The mercury alloys superficially with the platinum, and a film of platinum black is left when the mercury is dissolved. *W. D. B.*

The electrolytic determination of cadmium with the use of a rotating anode. *A. L. Davidson. Jour. Am. Chem. Soc.*, 27, *1275* (*1905*).—Ten electrolytes

were studied. Satisfactory results were obtained for cadmium with all except the lactate and the alkaline ammonium acetate solutions. Separations of cadmium from magnesium, iron, nickel and cobalt were made. The reviewer wishes that the theory of separations with a rotating anode could have been stated more clearly than in the following words:

"By the use of the high current densities, which are possible with a rotating anode, the separations, based upon differences of voltage, cannot be effected. Separations possible under these conditions are based upon the deposition or non-deposition of the separate metals from the electrolyte in which they are present together." *W. D. B.*

Determination of cadmium using a rotating cathode. *C. P. Flora. Zeit. anorg. Chem.*, 47, *1*, *13*, *20* (*1905*).—A description of experiments on the quantitative electrolytic precipitation of cadmium from all sorts of solutions, using a rotating cathode. *W. D. B.*

The rapid determination of lead in the electrolytic way. *R. O. Smith. Jour. Am. Chem. Soc.*, 27, *1287* (*1905*).—Lead peroxide was precipitated from an acidified lead nitrate solution, using a rotating cathode. It was shown that the peroxide deposits do not come to constant weight until heated at 230°.

W. D. B.

The rapid precipitation of antimony in the electrolytic way. *J. Langness and E. F. Smith. Jour. Am. Chem. Soc.*, 27, *1524* (*1905*).—Using a rotating anode and a solution of sodium sulphide to which potassium cyanide has been added, 0.2369 g antimony can be precipitated quantitatively in fifteen minutes. Antimony can be separated from arsenic in this solution. *W. D. B.*

Electrolytic preparation of nitrite from nitrate. *E. Müller and F. Spitzer. Zeit. Elektrochemie*, 11, *509* (*1905*).—If the potential necessary to reduce nitrate is lower than that necessary to reduce nitrite, it will be easy to obtain a relatively large yield of nitrite. If the reverse is the case, the reduction will proceed farther and no satisfactory yield of nitrite can be obtained. This reversal of potentials can apparently be effected by changing the material of the cathode. With smooth platinum nitrite is reduced, with spongy copper nitrate, and both with smooth copper. A copper salt plus a platinum cathode is even more effective than a spongy copper cathode. A silver cathode is much more effective than a copper cathode in causing the reduction of nitrate. Gold does not make a suitable cathode for the preparation of nitrite. This paper is an excellent illustration of Haber's dictum that the reaction determines the potential.

W. D. B.

Oxidation and reduction processes in the electrolysis of iron salt solutions. *Z. Karaoglanoff. Zeit. Elektrochemie*, 11, *489* (*1905*).—Experiments were made to test the possible use of ammonium iron alum in a coulometer, the ferrous iron to be titrated with permanganate. The ferrous salt is not oxidized by the air, but is readily oxidized at the anode. The author defines the 'critical' current density as the maximum density which does not set free visible amounts of hydrogen in two minutes. The critical density is proportional to the concentration of ferric salt; increases with rising temperature, and with addition of

various salts; and is greater with horizontal than with vertical electrodes. Since it also varies enormously with the rate of stirring, it probably has no more real significance than has the so-called maximum density for precipitating good copper. *W. D. B.*

Electrolytic reduction of oleic acid to stearic acid. *J. Petersen. Zeit. Elektrochemie*, 11, 549 (*1905*).—The cathode compartment contained aqueous alcohol, oleic acid and small amounts of hydrochloric acid. The efficiency of the reduction to stearic acid is low, 14–25 percent in most cases though sometimes running up to 60 percent. The efficiency increases the longer the oleic acid is left in contact with the hydrochloric acid, but no explanation for this could be found. The nature of the cathode appears to have little or no effect.

W. D. B.

Electrolytic formation of chlorate. *F. Foerster and E. Müller. Zeit. Elektrochemie*, 11, 502 (*1905*).—The authors take exception to Sirk's view (9, 607) that the catalytic action of the platinum electrodes is of importance in the electrolytic formation of chlorate. This hypothesis had been considered and rejected by the authors years ago. *W. D. B.*

Nickelic salts. *C. Tubandt. Zeit. anorg. Chem.*, 45, 73 (*1905*).—If a solution of potassium bicarbonate be electrolyzed, using a nickel anode, a reddish-brown solution of a nickel salt is obtained. A more concentrated solution can be prepared by starting with nickel carbonate dissolved in concentrated potassium bicarbonate. The nickelic salt is very instable and soon breaks down.

W. D. B.

Alkaline cobaltous oxide solutions. *C. Tubandt. Zeit. anorg. Chem.*, 45, 368 (*1905*).—A cobalt anode dissolves in caustic potash more readily the more concentrated the solution, the higher the temperature, and the lower the current density. The resulting blue solutions contain cobalt as cobaltous salt. The cobalt salt will not diffuse through parchment. On standing long enough, the hydroxide precipitates. The author considers that we are dealing with a colloidal solution. *W. D. B.*

The polysulphides. III. *F. W. Küster. Zeit. anorg. Chem.*, 46, 113 (*1906*).—When a concentrated solution of sodium sulphide is electrolyzed between platinum electrodes, sulphur is formed at the anode and then redissolves, giving rise to periodic phenomena. These have been studied by the author who gives a number of records of the fluctuations in current. *W. D. B.*

Potassium percarbonate. *W. D. Brown. Jour. Am. Chem. Soc.*, 27, 1222 (*1905*).—The author obtained a product containing only 30–40 percent potassium percarbonate as against 80–95 percent obtained by Constam and von Hansen. He thinks that sodium peroxide is more useful for all purposes than potassium percarbonate. *W. D. B.*

The behavior of magnesium anodes. *G. Baborovsky. Zeit. Elektrochemie*, 11, 465 (*1905*).—When magnesium is made anode in chloride or sulphate solution a black precipitate forms which was considered by Beetz to be a suboxide. It proved impossible to prepare this substance in a state of purity even by using

alcoholic potassium acetate solutions and the author believes that it is a mixture of magnesium and magnesium oxide. In chloride the anode is about one and a half times the theoretical, corresponding to an apparent valency of 1.33 instead of 2.0. In alkaline solutions the anode loss is less than one-fourth the theoretical, but, for some unknown reason, the author prefers to speak of 100 percent efficiency with a valency of nine. Electromotive force measurement showed a fairly constant potential which was independent of the concentration of magnesium as ion. *W. D. B.*

Cathodic disintegration of tellurium. *E. Müller and R. Lucas. Zeit. Elektrochemie*, 11, 521 (*1905*).—The authors have studied the formation of tellurium hydrosol by the cathodic disintegration of tellurium. They consider this to be the result of a changing valency, analogous to the disintegration of a copper anode under certain circumstances. Their next conclusion is that all cathodic disintegrations come under this head. *W. D. B.*

Dielectricity and Optics

Preparation of oxides of nitrogen by high tension discharges in air. *O. Scheuer. Zeit. Elektrochemie*, 11, 565 (*1905*).—The author has studied the formation of nitric acid from atmospheric nitrogen, paying attention to the effect of watts supplied; distance between electrodes; shape of vessel; manner of leading in air; shape of electrodes; nature of electrodes; moisture. The experiments were made with a Ruhmkorff coil and with an alternating current high-tension transformer. The nature of the electrodes has no effect and the loss in weight of platinum electrodes is so much less than that for other electrodes, as more than to counterbalance the difference in cost. In moist air, the author believes that unknown oxides of nitrogen are formed to some extent. *W. D. B.*

The coloring of halides of the alkalies and the alkaline earths. *L. Wöhler and H. Kasarnowski. Zeit. anorg. Chem.*, 47, 353 (*1905*).—The authors believe that the blue color of natural rock salt is due to organic matter and not to sodium as in the case of the coloring by means of cathode rays. The color disappears at different temperatures in the two cases and shows different intermediate shades. No free alkali can be detected when the rock salt is dissolved. A similar difference occurs between the two colored fluorspars. *W. D. B.*

THE VAN'T HOFF-RAOULT FORMULA

BY WILDER D. BANCROFT

By means of a thermodynamical cycle involving the use of a semipermeable piston, van't Hoff deduced in 1885 an equation[1] which can be written in the form

$$PV = RT\frac{N}{n}\log\frac{p_o}{p_1}.$$

In this equation P is the osmotic pressure, V the volume through which the piston moves in squeezing out the amount of solvent in which one molecular weight of the solute is dissolved, R is the gas constant, T is the absolute temperature, n is the grams of solute divided by the molecular weight of the solute in the solution, N is the grams of solvent per molecular weight of solute divided by the molecular weight of the solvent when in the form of vapor, p_o is the vapor-pressure of the pure solvent at the temperature T, while p_1 is the partial pressure of the solvent in the solution at the same temperature.

In deducing this equation the assumptions were made that the vapor of the solvent followed the gas law and that the volume of the liquid could be neglected in comparison with that of the vapor when calculating the work done in an isothermal distillation. No other assumption is involved and the formula must be absolutely accurate except in so far as corrections due to the two explicit assumptions have to be made. The value of these corrections is easily determined in any particular case.

It is to be noticed that the volume V is not the molecular volume of the solution except for solutions[2] so dilute "that the volume occupied by the molecules of the solute is negligible in comparison with the volume of the solution."

[1] Kongl-Svenska Vetenskaps-Akademiens Handlingar, 21, 3 (1886); Zeit. phys. Chem., 1, 481 (1887).

[2] van't Hoff: Zeit. phys. Chem., 1, 483 (1887).

For two liquids such as carbon tetrachloride and benzene which are miscible in all proportions without contraction or expansion,[1] V will be the volume of the liquid which passes through the piston. If we mix 78 grams of benzene (about 68.6 cc at 20°) and 154 grams of carbon tetrachloride (about 245 cc at 20°) the volume V at 20° will be 245 cc in case the piston is permeable to carbon tetrachloride only and 68.6 cc in case it is permeable to benzene only. In neither case will it be 313.6 cc, the molecular volume of the solution. The usual definition of osmotic pressure is that it is the pressure which the solute would exert if it were present as a gas at that temperature, the volume being that of the solution. If we cling to this definition we cannot hold to the van't Hoff-Raoult formula

$$\frac{n}{N} = \log \frac{p_0}{p_1}$$

because the amount of solvent to be squeezed out is no longer N/n. If we stick to the van't Hoff formula, the osmotic volume becomes a physical fiction in some cases because it is difficult to think of 154 grams of carbon tetrachloride occupying a volume of 68.6 cc when no pressure we can apply would be sufficient to compress carbon tetrachloride into that volume either as liquid or as solid.

In spite of this difficulty the wise thing to do is to take the osmotic volume as defined by van't Hoff. An interesting confirmation of this is found in Cohen's[2] work on the inversion of cane sugar. Satisfactory results were obtained only when the concentration of cane sugar was referred to the volume of the water and not to the volume of the solution. Quite recently Morse and Frazer[3] have shown that their direct measurements of osmotic pressure come out better when the concentrations are referred to a constant volume of solvent. They consider this a discovery of their own, quite overlooking

[1] Brown: Jour. Chem. Soc., 39, 202 (1881).
[2] Zeit. phys. Chem., 33, 442 (1897).
[3] Am. Chem. Jour., 34, 1 (1905).

the fact that they have simply gone back to van't Hoff's original formulation. Having reached their conclusion empirically, Morse and Frazer have also overlooked that their method of expressing concentrations contains the tacit assumption that there is neither expansion nor contraction when the two components are mixed. For the general case we have the relation

$$V = \frac{NM_2}{n}\frac{\partial V}{\partial m_2},$$

where M_2 is the molecular weight of the solvent as vapor and $\frac{\partial V}{\partial m_2}$ the change in volume when 1 gram of the solvent is added to an infinitely large mass of the solution. In this paper V will always have this significance.

Returning to the original equation

$$PV = RT\frac{N}{n}\log\frac{p_0}{p_1},$$

we can obtain the van't Hoff-Raoult formula

$$\frac{n}{N} = \log\frac{p_0}{p_1}$$

by postulating the relation PV=RT. The conditions under which we may do this have been stated clearly and explicitly by van't Hoff. This relation can hold only in case the heat of dilution is negligible.[1] At that time it was important to test the simplest case and for infinitely dilute solutions the heat of dilution is negligible.

In 1894 Ewan[2] took up the problem again and worked out a formula for the relation between osmotic pressure and heat of dilution. This formula was said by the author to apply only to cases in which no dissociation and no chemical combination occur. This decreased the value of the paper very much because there is no way at present by which one can tell to what the heat of dilution is due. In consequence of

[1] Kongl-Svenska Vetenskaps-Akademiens Handlingar, 27, 13 (1886).

[2] Zeit. phys. Chem., 14, 417 (1894); 31, 22 (1899).

this and of a bad agreement between experiment and theory, these investigations of Ewan have fallen into undeserved oblivion. In 1898 Cady[1] found that sodium amalgam concentration cells gave electromotive forces which indicated abnormally low molecular weights. He showed that these peculiar results were due to the heat of dilution. He also showed that his results ran parallel with those of Ramsay[2] on the vapor-pressures of sodium amalgams; but he was not able to treat the simple case of the vapor pressures quantitatively. The general formulation, applicable to all cases, has recently been given by Trevor.[3]

The following derivation, also due to Trevor, seems t me more intelligible. Under all circumstances, for any fixed concentration, we have the relation

$$PV = Q + T\frac{d(PV)}{dT}$$

where Q is taken as positive if heat is evolved when the solution is diluted. This can be integrated if we know Q as a function of T. When Q is zero, the formula becomes

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} = \text{const.}$$

Experiment shows that one particular solution is the right one, namely

$$PV = RT.$$

When Q is independent of the temperature and is equal to a constant, A, we have

$$\frac{P_1V_1 - A}{T_1} = \frac{P_2V_2 - A}{T_2} = \text{const.}$$

In view of our experience with the previous case we adopt the particular solution

$$PV = RT + A.$$

If we assume that $Q = A - BT$ and adopt the same solution we have

$$PV = RT + A + BT \log T.$$

[1] Jour. Phys. Chem., 2, 551 (1898).
[2] Jour. Chem. Soc., 55, 521 (1889).
[3] Jour. Phys. Chem., 9, 90 (1905).

We could go on indefinitely, assuming that Q was different functions of T; but these three cases are enough to show the method.

Having established a relation between the osmotic pressure and the heat of dilution, it is now necessary to inquire what heat of dilution comes into the formula. From the van't Hoff deduction we see that the heat effect is that caused by the addition of N/n molecular weights of the solvent to an infinitely large mass of solution. This cannot be measured directly; but it is possible to get round the difficulty. If the heat of dilution be expressed, as is usually done, with reference to the molecular concentration, N/n, the heat required in the van't Hoff formula is given by the relation[1]

$$Q_H = \frac{\partial Q}{\partial\left(\frac{N}{n}\right)} \frac{N}{n}$$

$$Q_H = \frac{\partial Q}{\partial C} C$$

where C denotes the number of molecular weights of solvent per molecular weight of solute.

In this discussion Q_H has been taken as positive when there is an evolution of heat on diluting the solution. In any case where we have a marked evolution of heat on dilution we shall expect to find an abnormally high osmotic pressure and to calculate an abnormally low molecular weight. The first instance of this is sodium in mercury. Ramsay[2] found apparent molecular weights for sodium in mercury varying from 21.6 in dilute solutions down to 15.1 in the most concentrated. Cady[3] has measured the heat of dilution when a solution containing 20.2 molecular weights of mercury per molecular weight of sodium is changed to one containing 86.7 molecular weights of mercury per molecular weight of

[1] I propose the symbol Q_H to denote the van't Hoff or osmotic heat of dilution.

[2] Jour. Chem. Soc., 55, 533 (1889).

[3] Jour. Phys. Chem., 2, 562 (1898).

sodium. While this is altogether too wide a range over which to draw a tangent, we shall probably not be much in error if we assume that the mean value of $\Delta Q/\Delta C$ or 13.2 gram-calories is not far from the value of $\partial Q/\partial C$ for the concentration measured by Ramsay of 35.8 molecular weights of mercury per molecular weight of sodium. Assuming this and assuming that the heat of dilution is independent of the temperature, as shown by Cady for a short range, we get the following interesting result:

TABLE I

Apparent molecular weight of sodium.....	16.5
Correction for heat of dilution.....	6.2
Corrected molecular weight of sodium.....	22.7

Solutions of sulphuric acid in water show very large heats of dilution and correspondingly low apparent molecular weights. In Table II the first column gives the concentrations in molecular weights of water per molecular weight of sulphuric acid. In the second column are Dieterici's vapor pressure measurements at 0°. In the third column are the osmotic heats of dilution. Those in the upper part of the table are based on Ewan's interpolations from Pfaundler's measurements[1] while those in the lower part are based on Nernst's interpolations from Thomsen's results.[2] Nernst[3] believes that these heats of dilution may be considered as practically independent of the temperature. In the fourth column we have the apparent molecular weights calculated in the ordinary way. In the fifth column are the values obtained on the assumption that Q_H is independent of the temperature.

[1] Zeit. phys. Chem., 14, 417 (1894).
[2] Theor. Chem. 3rd Ed., 164.
[3] Ibid.

TABLE II

Dieterici, Pfaundler, Ewan

N/n	mm Hg.	Q_H	App. M. W.	Corr. M. W.
91.6	4.535	299	57.7	89.5
53.5	4.452	520	49.2	96.4
29.2	4.284	877	44.5	116.3
20.8	4.065	1183	36.9	117.4
14.7	3.664	1581	28.9	113.0
11.3	3.238	1928	24.4	111.3
9.9	2.952	2128	22.0	108.5

Dieterici, Thomsen, Nernst

91.6	4.535	363	57.7	96.1
29.2	4.284	978	44.5	124.3
14.7	3.664	1739	28.9	121.0
9.9	2.952	2322	22.0	116.6
5.9	1.679	3215	16.4	113.1
4.8	1.206	3551	15.3	115.2
2.5	0.164	5073	11.7	104.8

With increasing concentration of sulphuric acid, the apparent molecular weight drops rapidly from 57.7 in a 5.6 percent solution to 11.7 in a 68.5 percent solution. If we introduce the correction due to the heat of dilution, this absurdity disappears and we get molecular weights increasing at first with increasing concentration and then remaining approximately constant. Owing to the inaccuracy of the thermal data and to the possibility that they may vary somewhat with the temperature, no importance can be attached at present to the fluctuations of the corrected molecular weight between 124 and 105. On the other hand, it is very gratifying to get so good a result over so wide a range of concentrations.

Beckmann's measurements[1] on resorcinol in alcohol show a molecular weight decreasing with increasing concentration. For concentrations of 0.1972, 0.5119 and 1.0375 grams resorcinol per 9.19 grams alcohol, the apparent molecular weights were 108, 105 and 100 respectively, the formula

[1] Zeit. phys. Chem., 8, 227 (1891).

weight being 110. Speyers[1] worked with the air-bubbling method and obtained an apparent molecular weight of 58.7 at 30° for a solution containing 20.3 grams resorcinol and 20.4 grams alcohol. Speyers[2] also showed that alcohol solutions of resorcinol evolve large amounts of heat when diluted.

The molecular lowering of the freezing-point of solutions of cupric chloride in water increases with increasing concentration.[3]

As a type of the reverse case in which there is a marked absorption of heat on dilution and a correspondingly high apparent molecular weight we may take solutions of ethyl alcohol in benzene. Beckmann[4] has found that the apparent molecular weight of ethyl alcohol increases from 45.9 to 318 as the concentration increases from 0.164 gram to 32.45 grams alcohol per 100 grams benzene. It has been shown by J. W. Walker[5] that there is a very marked absorption of heat when solutions of alcohol in benzene are diluted. The heat absorption is so great that we come out with impossible results if we assume that it is independent of the temperature. It is to be hoped that Mr. Walker will determine the heat-concentration curve for several temperatures so that we may be able to express the heat of dilution as a temperature function.

So far, we have been considering exceptional cases in which the heat of dilution is very large and the concentration relatively high. It may well be asked what is the value of the correction for dilute solutions and for the solutes most often studied. Calculation shows that at 0° the apparent molecular weight may be in error 10–15 percent if there is a heat effect of 1 gram calorie when 1 liter of pure solvent is added to 1 liter of a $n/100$ solution. Small as this heat effect is, it is larger than what actually occurs in most solutions. From the tabulated heats of dissociation of electrolytes,[6]

[1] Am. Jour. Sci. (4), 13, 213 (1902).
[2] Jour. Am. Chem. Soc., 18, 146 (1896); Am. Jour. Sci. (4), 10, 449 (1900).
[3] Rüdorff: Pogg. Ann., 116, 70 (1862).
[4] Zeit. phys. Chem., 2, 728 (1888).
[5] Trans. Roy. Soc., Canada, 8, III, 105 (1902).
[6] Landolt-Börnstein: Meyerhoffer Tabellen, 466.

we see however that heat effects of one-tenth to one-twentieth this value are quite common. At 0° the apparent molecular weights of potassium chloride, potassium bromide and hydrochloric acid may easily be in error from 0.5 to 1.5 percent in $n/100$ solutions. Under these circumstances, it is a waste of time to speculate about variations from the dilution law until we have eliminated the known errors in the determinations. It is quite possible that the difference between strong electrolytes and weak organic acids is due chiefly to a difference in the heats of dilution.

Practically all calculations of the electromotive forces of concentration cells are in error to a greater or lesser extent because Nernst's formula is based on the assumption that the heat of dilution is zero. All calculations as to the existence of hydrates in concentrated solutions are also in error because they are based on the apparent molecular weights which are themselves necessarily wrong. This criticism does not affect the existence of hydrates in solution. It merely emphasizes the fact that formulas assigned to account for erroneous molecular weights cease to have any justification as soon as it is recognized that the molecular weights in question are wrong.

In connection with this we must consider the case of sodium chloride and water. While sodium in mercury, sulphuric acid in water, resorcinol in alcohol, and alcohol in benzene behave as they should, sodium chloride in water shows a decreasing apparent molecular weight with increasing concentration[1] in spite of the fact that there is an absorption of heat when the solution is diluted. The correction, which must be applied, will make the molecular weights more unsatisfactory than they now are. The only way out of the difficulty seems to be to assume that, owing to the formation of hydrates in solution, the apparent concentrations are very different from the real ones.

Under certain circumstances we may have an abnormally

[1] Kahlenberg: Jour. Phys. Chem., 5, 362 (1901).

low molecular weight even though there is an absorption of heat on dilution. If $Q_H = A - BT$ we have $PV = RT + A + BT \log T$. When $T_1 = A/B$, Q_H is zero and $PV = RT + A + A \log T$. In this case we have an abnormally high osmotic pressure even though the heat of dilution is zero for the temperature T_1. When $T_1 > A/B$, the heat of dilution changes sign but the osmotic pressure is higher than the normal and the molecular weight lower than the normal. Sodium chloride and water do not come under this head though there is some reason to suppose that resorcinol and alcohol may at higher temperatures.

We must now face another question. If an apparent molecular weight of 15 or less for sodium in mercury means a real molecular weight of 23, what does an apparent molecular weight of 29.3 mean for sodium chloride in aqueous solution? There is one fundamental difference between the two cases. The apparent molecular weight of sodium in *mercury is 23 for infinite dilution* so that it then agrees with the formula weight. For infinite dilution the apparent molecular weight of sodium chloride is 29.3 or half the formula weight. At infinite dilution the change of the heat of dilution with the concentration becomes zero and the correcting term becomes zero. The apparent molecular weights at infinite dilution are therefore true molecular weights. Since we must postulate a dissociation for sodium chloride in dilute aqueous solution, there is no point in postulating anything except an electrolytic dissociation. We come back to the conclusion that the electrolytic dissociation theory must hold absolutely for infinite dilution, which is exactly what experiment has shown. On the other hand we see that all determinations in finite solutions have been in error by amounts varying from a fraction of a percent up to several hundred percent. All of our experiments, which involve molecular weights in solution, must be redetermined. While this seems a bit discouraging at first sight, it must be kept in mind that when we have done this we shall probably be able to break loose from the tyranny

of dilute solutions and to develop a quantitative physical chemistry which shall apply to all concentrations.

We can now reconcile Kahlenberg's point of view with that of the orthodox physical chemist. Kahlenberg has worked with finite solutions and has found that one must consider the specific nature of solvent and solute. The majority of physical chemists have worked with very dilute solutions and have obtained results which were independent of the nature of solvent and solute—within certain limits. For finite solutions the heat of dilution is a factor and it varies with the specific nature of solvent and solute, just as Kahlenberg has found. For infinitely dilute solutions, the heat of dilution becomes negligible and the effects due to the specific nature of solvent and solute become unimportant—within certain limits. Kahlenberg has not really been fighting the electrolytic dissociation theory. He has been fighting the false applications of the electrolytic dissociation theory, and there have been many of these.

The general results of this paper are:

1. It has been shown how the osmotic pressure varies with the heat of dilution.

2. The abnormal molecular weights for sodium in mercury, sulphuric acid in water, resorcinol in alcohol, cupric chloride in water, and alcohol in benzene are due wholly or in part to the heats of dilution.

3. The abnormal molecular weights for sodium chloride in water are not due to the heat of dilution.

4. The molecular weights at infinite dilution are correct but all others are in error to a greater or lesser extent.

5. It is probable that a quantitative theory of concentrated solutions can be worked out if we make corrections for the heat of dilution.

Cornell University,
December, 1905.

THE MOLECULAR AGGREGATION OF LIQUEFIED GASES[1]

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In recent years no branch of the science of Physical Chemistry has been so thoroughly investigated as that of solutions. In consequence of these investigations we are now in a position to lay down as one of the fundamental laws of solution the following rule:

"That the vapor pressure of a liquid is lowered by the addition of a non-volatile substance; that the lowering is proportional to the amount of substance dissolved, and that, in one and the same solution, the lowering at any temperature bears always a fixed ratio to the vapor pressure of the pure solution at that temperature."

The experimental verification of this rule was first made for aqueous solutions by von Babo[2] (1848) and Wüllner[3] (1856) and was later extended by Tammann[4] (1885) and Emden[5] (1887).

But we are indebted chiefly to Raoult[6] for the most exact application of this law. As a result of his investigations Raoult has enunciated the following rule. "At equal temperatures the depression of the vapor pressure of a liquid is proportional to the ratio of the number of molecules of dissolved substance to the total number of molecules in solution."

If then at any given temperature, p be the vapor pressure of the solvent, p^1 that of the solution, N and n the number of molecules of solvent and of dissolved substance respectively,

[1] Being part of a thesis presented to the examiners for the Doctor of Science in the University of London.

[2] von Babo: Jahresber. f. Chem., Vol. I. 1848, 10, 1857.

[3] Wüllner: Pogg.-Ann., 103, (1856); 110, (1860).

[4] Tammann: Wied.-Ann., 24, (1885).

[5] Emden: Wied.-Ann., 31, 1887.

[6] Raoult: Comptes rendus, 1878, 1886-1890, Annales de Chim. et de Phys. (6), 1888-1890.

then $$\frac{p - p^1}{p} = \frac{n}{n + N} \qquad \text{I}$$

This law has been found to be generally true for all solvents at ordinary temperatures; occasional lapses from conformity are explained by the association or dissociation of one or other of the substances concerned.

The application of the law was next further extended by Ramsay[1], who proved that the same relation held at higher temperatures when mercury was used as a solvent and other metals were in turn dissolved in it.

There remained, then, but one direction in which to extend the observations, *viz.*, to low temperatures with liquefied gases as the substances used. To this end experiments were begun on the change produced in the vapor pressure and boiling point of liquefied gases when other gases are dissolved in them.

There are two methods open to us in the investigation. We may determine,

(*a*) the lowering of the vapor pressure at constant temperature,

(*b*) the rise of boiling-point at constant pressure of the pure solvent by the presence of a dissolved substance.

The former or static method was that first used by Raoult[2] in his investigations. The second or dynamic method was introduced by Beckmann[3] to obviate the unavoidable changes in concentration which vitiated Raoult's results.

1. Lowering of Vapor Pressures

The equation I above may be written

$$\frac{p - p^1}{p^1} = \frac{n}{N} \qquad \text{II}$$

i. e., the ratio of the lowering of vapor pressure to the vapor pressure of the solution is equal to the ratio of the number of molecules of solute to the number of molecules of solvent.

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[1] Jour. Chem. Soc., 55, 521 (1889).
[2] Ann. Chim. Phys. (6), 1888, 1890.
[3] Zeit. phys. Chem., 4, 532 (1889); 6, 437 (1890).

If now we take known volumes of two gases, we know, from Avogadro's hypothesis, the ratio of the molecules of these two gases present; and if, further, we condense these gases and determine the lowering of the vapor pressure produced by the mixture, we have then from Raoult's law another ratio, *viz.*, that of the number of molecules present in the liquid state.

We have thus a possible means of establishing a correlation between the molecule aggregation of gases in the gaseous and liquefied states.

In such experiments the solute must obey one essential condition: it must have no appreciable vapor pressure at the temperature of the experiment. If otherwise, a complication is introduced into the experiment and Raoult's simple law can no longer hold. This circumstance then must restrict the number of substances which are available for experiment.

1. Apparatus

The apparatus used in the experiments to be later detailed is represented in the accompanying sketch.

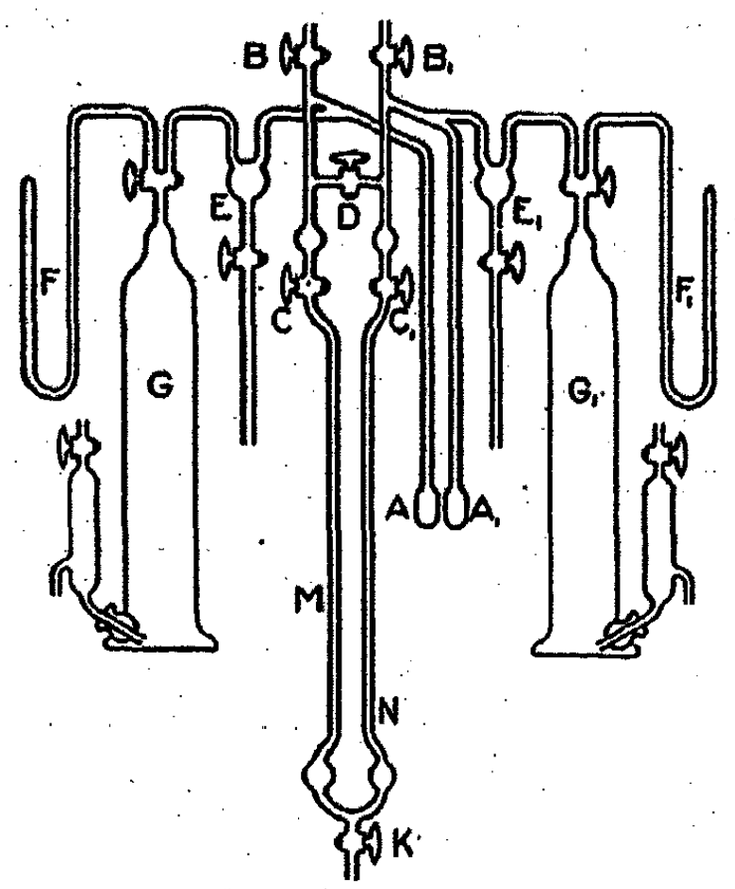


Fig. 1.

Two small tubes A and A_1 of a capacity of three cubic centimeters were placed as close together as possible and were connected each to one side of the oil manometer M. This manometer was constructed of glass of about 5 mm bore and its length along the parallel arms was 200 ccm. The tap K served to introduce the liquid to be used in the manometer and the taps C and C_1 to cut off the manometer from the rest of the apparatus. For this purpose a tap was first introduced at N; but the action of the oil on the tap grease used to lubricate the tap soon caused the tap to leak and break the column of the oil in the manometer by introducing bubbles of air. The tap D served as a communicating tap between the two sides of the apparatus. The gases were introduced through the capillary U tubes F and F_1 into the gas cylinders G and G_1 and thence transferred to the apparatus— any mercury, which was carried over in so doing, being retained in the mercury traps E and E_1. The taps B and B_1 were connected one to each side of the apparatus and served as connection with a Toepler pump.

By this means either side of the apparatus or both simultaneously could be readily evacuated.

The method of conducting experiments was as follows. The taps B, C and D were first opened. The apparatus was then exhausted by means of a mercury pump and was allowed to stand for an hour with the taps B and B_1 closed, to test if the apparatus were air tight.

The taps C, C_1 and D_1 were then closed. The substance to be dissolved in the solvent was introduced into G and transferred to the left side of the apparatus. Then by means of the liquid air this gas was frozen solid on the bottom of the bulb A. Equal volumes of the solvent were then introduced into A and A_1 and liquefied by the liquid air in the vacuum vessel, which now surrounded the bulbs. When these had been left for some ten minutes, the taps C and C_1 were opened simultaneously and the deflection of the oil in the manometer was read off on a 200 cm Zeiss scale placed immediately in front of the parallel limbs.

The oil used in the manometer was the high boiling Fleuss oil (sp. gr. 0.87) supplied by the Pulsometer company for vacuum pumps. This oil, after standing in an evacuated flask immersed in boiling water for an hour, gave off no bubbles of gas on standing in the evacuated manometer.

To complete the experiment a third bulb placed in the rear of A and A_1 was connected with an absolute mercury manometer and an apparatus similar to I and G for introducing the gas. This was filled on each occasion with a sample of the gas used as the solvent; an absolute value (p) for the pressure of the gas used at the temperature of the experiment was thus obtained.

Now by converting the difference in pressure observed on the oil manometer into mercury units and dividing this by the absolute vapor pressure of the pure solvent, we can obtain (from equation I) a value of the ratio for the number of molecules of the gases under experiment in the liquefied state.

2. Preparation of Gases

Oxygen.—Prepared by heating potassium permanganate. Carbon dioxide was removed by soda lime and moisture by phosphorus pentoxide.

Methane.—By heating sodium acetate (one part) and soda lime (three parts). The gas was purified by condensing by means of liquid air about thirty liters of the gas. The low boiling gases were then pumped off till the amount removed by each stroke of the pump remained constant. The liquid was then allowed to evaporate slowly. The first ten liters of gas were taken and again fractionated, when the first portion proved to be pure methane.

Ethylene.—By heating alcohol and sulphuric acid. To purify the gas it received a preliminary washing with aqueous caustic potash. In the course of the experiments it stood in a gas cylinder over water for three months. To prepare the pure gas for experimentation, some of this impure gas was condensed in liquid air. The volatile gases were then pumped completely away and the solid ethylene allowed to evaporate. The first 100 cc on evaporation was allowed to enter the pump.

The next fraction was collected and proved to be pure ethylene.

Ethane.—Prepared by electrolysis of a saturated solution of sodium acetate to which had been added a little acetic acid. The gas escaping from the positive pole was washed with aqueous caustic potash and fuming sulphuric acid to remove carbon dioxide and ethylene. This gas was then purified by fractionation.

Acetylene.—From calcium carbide and water. The gas evolved was repeatedly washed with an acidified solution of copper sulphate till no further precipitation took place, then passed over soda lime and phosphorus pentoxide and finally purified by fractionation.

Carbon dioxide.—From purified sodium carbonate and dilute sulphuric acid; purified by fractionation.

Sulphur dioxide.—The gas from a liquid sulphur dioxide cylinder was condensed in liquid air, the volatile constituents removed by pumping and the soild then allowed to evaporate.

Nitrous oxide.—The gas from the nitrous oxide cylinders was condensed in the usual way and the nitrogen present removed by pumping off the volatile constituents at the temperature of liquid air.

Nitric oxide.—Prepared by the action of acetic acid on a mixture of potassium ferrocyanide and potassium nitrate.

Sulphuretted hydrogen.—By the action of dilute sulphuric acid on calcium sulphide. This latter substance was made by the reduction in a closed furnace of calcium sulphate by starch carbon.

Phosphoretted hydrogen.—From calcium phosphide and dilute hydrochloric acid. The gas was first passed through a tube immersed in ice and salt, then condensed in liquid air and fractionated as above.

Measurement of Volumes

The volumes of the gases used were measured in a Huntley constant volume burette (vide Travers': "Study of Gases," p. 69). The apparatus there described was modified by im-

mersing both burette and barometer in a single water jacket, the sides of which were wood, the front and back of glass.

For larger quantities of gas than could be dealt with in the Huntley burette, Julius Thomsen's method (Ibid; p. 72) was adopted.

3. Results

Although every precaution was taken in experimentation, the results obtained with the apparatus, as described, were not as good as might have been expected.

The first possibility of error arose from the unequal heating of the bulbs containing the liquids. To avoid this as much as possible the liquid air which was used as a bath was first stirred by bubbling hydrogen through it. It was, however, found soon that this in itself could cause rapid variations in the oil manometer according as the bubbles of hydrogen (which did not rapidly enough assume the temperature of liquid air), arose round one or other of the bulbs. Finally an automatic stirrer was arranged and kept in continuous motion.

The second difficulty, which proved even more difficult to overcome, arose from the variations in surface concentration of the solutions. The trouble was only partially obviated by a continuous tapping of the bulbs. In some experiments small glass fragments were placed in the bulbs which, on tapping, caused an agitation of the solution; in others a piece of platinum foil was used for a like purpose. But with every device that could be tried the experiments were irregular and inconsistent.

I first attempted to dissolve nitrogen monoxide and ethylene in succession in oxygen. The methane was used as solvent and ethylene and phosphine (PH_3) were dissolved in it. Then ethylene was tried with sulphur dioxide and acetylene. But the results were so inconsistent that after five months' experimentation seeing that the results of even the best regulated experiments showed inconsistency among themselves, I came to the conclusion that further investigation in this direction was useless.

The utility of the experiments performed lies only in the proof which they afford that all gases under consideration are to some extent soluble in one another. This is of direct interest in the later work where it will be shown that the number of the commoner gases which are soluble in one another to the extent of more than one percent is extremely limited indeed.

My next move was then to attempt the solution of the problem from the second direction previously mentioned on page 331 *viz.*, by observations of the boiling points of the solutions at constant pressure. The variations in surface concentration which appear to be at the bottom of all the trouble are then avoided by stirring the liquid with bubbles of its own vapor.

II. RISE OF BOILING-POINT

A. Theoretical Considerations

The mechanical theory of heat gives us the following formula (Clapeyron's equation)

$$\frac{dp}{dT} = \frac{\lambda}{(v - v_1)T} \qquad \text{III}$$

for the relation between pressure, volume and temperature of a gas where T is the absolute temperature at which the vapor pressure is p, λ is the heat of vaporization of one gram molecule of the liquid and v and v_1 the volumes occupied by one gram molecule in the gaseous and liquid states. Now combining this with the gas equation

$$pv = RT$$

and neglecting the value of v_1 as being small compared to v, we get

$$\frac{dp}{dT} = \frac{\lambda p}{RT^2}$$

i. e.,

$$\frac{p - p'}{p} \cdot \frac{RT^2}{\lambda} = dT$$

and since by Raoult's law $\frac{p - p'}{p} = \frac{1}{n}$

where n is the ratio of the number of molecules of solution to the number of molecules of solute, then

$$d'T = \frac{1}{n} \cdot \frac{RT^2}{\lambda}$$

and since the value of the constant R = 2 when λ is expressed in calories, then

$$d'T = \frac{1}{n} \cdot \frac{2T^2}{\lambda}^1 \qquad \text{IV}$$

In determining the rise of boiling-point produced by the solution of one substance in another, we can readily obtain values for all the unknowns on the right side of this equation with the exception of λ. Now values of λ in the cases of all the solvents used have been obtained by substituting in Clapeyron's equation (III) values for $\frac{dp}{d'T}$ taken from the vapor pressure curves of the liquids.

In the case of methane the vapor pressure curve had to be experimentally determined (vide appendix I), while values for the vapor pressure of oxygen were obtained from Travers' results.[2]

If, for example, we wish to determine the rise of boiling point of pure methane in the neighborhood of 97° (Abs) produced by the addition of one percent of another substance we proceed as follows:

From the vapor pressure curve of methane we take the following numbers

T (Abs)	press	$\frac{dp}{d'T}$
96°	190 mm	23 mm = 2.3 × 13.6 grams.
97°	213 mm	

Now from equation III $\lambda = \frac{dp}{d'T} \cdot T. v$ c. g. units

$$= \frac{dp}{d'T} \cdot \frac{T.v}{42500} \text{ calories}$$

[1] Vide Arrhenius: "Electrochemistry," p. 49 (1902 edition).
[2] Phil. Trans. 200 A, 152 (1903).

and since v the volume of one gram molecule at 97° (Abs) and 213 mm press $= \frac{22400 \times 760 \times 97}{213 \times 273}$ cc.

Then

$$\lambda = \frac{2.3 \times 13.6 \times 97 \times 22400 \times 760 \times 97}{42500 \times 213 \times 273}$$

$$= 2026 \text{ calories}$$

and since for one percent concentration (from equation IV)

$$dT = \frac{1}{100} \cdot \frac{2 \times (97)^2}{2026}$$

$$= 0.093 \text{ degree}$$

The values of dT for one percent concentrations calculated after this method are tabulated below:

METHANE:

Temp. absolute	Press.	$\frac{dp}{dT}$	λ	dT
97	213	2.3	2026	0.093
100	302	3.1	2062	0.097
110	750	6.9	2152	0.112

OXYGEN:

87	536	5.9	1677	0.090
90	744	8.3	1810	0.089

Thus, in the case of liquefied gases dissolved in one another, a one percent gram molecular concentration of the solute should raise the boiling point of the solvent about 0.1 of a degree.

B. Practical Manipulation

In order to determine experimentally the rise in boiling-point produced by the solution of one liquefied gas in another, two thermometers were used. The first of these to be described is the Resistance Thermometer, the second an iron-constantan thermocouple. The former was always used in experiments in which the volume of liquid used amounted to more than 10 cc or in those in which the temperature of the bath in which the liquid was immersed was to be taken; the latter was ex-

clusively used in experiments on the rise of boiling points of liquids, when the volume of the liquid was often as small as 3 cc.

a. Platinum Resistance Thermometer

In the construction of this thermometer a length of 1 meter of platinum wire of a diameter of $^1/_{10}$ mm, doubly insulated with silk, was wound on mica vanes in the usual way. The silk winding on the wire allowed the thermometer to be made much more compact than those in general use, though at the direct expense of the sensitiveness of the instrument. The pyrometer and compensating leads were made of stouter copper wire of about 1 mm diameter. The resistance of the platinum wire was determined by connecting the leads with a Callendar recorder. This instrument was worked by placing two ordinary storage cells to work the electro-magnets and one cell on the Wheatstone bridge. By this means the current flowing through the thermometer wire was kept as low as possible and the heat disturbance thereby reduced to a minimum.

(For the application of platinum thermometry vide Callendar Phil. Trans A 1887, Phil. Mag. July 1891, July 1892, Feby 1899.)

Calibration of the Thermometer

The thermometer was calibrated as follows :

	Ohms	Temp.
Resistance in ice	7.703	0°C
in steam (hypsometer)	10.532	100.3 (Atm. press 767 mm)

$\therefore$ fundamental coefficient of wire $= \frac{2.829}{7.703 \times 100.3} = 0.00362$

and absolute zero of wire $= \frac{1}{0.00362} = -273.1$ °C.

The thermometer was then placed in the liquid air, the temperature of which was simultaneously observed by an oxygen manometer.

Resistance 1.988 ohms

Temp (t) -190.4 °C

$\therefore$ "pt" (the platinum temp. for liquid air)

$= \frac{5.715 \times 100.3}{2.829} = -202.6$ degrees

and $t - pt = 12.2$ degrees

Then the value of δ in Callendar's difference formula from the equation

$$t - pt = \delta\left(\frac{t}{100} - 1\right)\frac{t}{100} \qquad \text{V}$$

is 2.21.

With these data we are now in a position to measure any temperature within the range from 100° C to —190° C. We have first to find the resistance of the thermometer in the liquid in question. Then we can calculate "*pt*" the platinum temperature of the liquid for

$$pt = \left(\frac{R_t - R_o}{R_{100} - R_o}\right) \times 100 \qquad \text{VI}$$

where R_t is the resistance at the temperature to be determined, R_o and R_{100} the resistance at zero and 100° C respectively.

Then from the difference formula (equation V) we can find the true temperature *t*.

To prove the accuracy of the thermometer at intermediate temperatures I determined the temperature of a mixture of carbon dioxide and alcohol with the following result.

Resistance of thermometer	5.412 ohms
pt temperature	—81.2 °C
t "	—78.12 °C.

But Olszewski and also Travers have determined the temperature of carbon dioxide and alcohol to be —78.2° C; so that the error of interpolation is less than 0.1° C.

The values for $t - pt$ and *t* were then plotted as ordinates and abscissae on a diagram and the curve for the corresponding values of *pt* and *t* were drawn (vide Callendar Ibid).

We have thus, in determining temperature, to find the resistance of the wire, then to calculate *pt* from equation VI and finally to read off *t* from the plotted curve.

b. Iron Constantan Thermocouple

The junction of the thermocouple was made by fusing the iron and constantan wires by means of an oxyhydrogen blowpipe. These wires were in turn joined to copper leads and

these junctions were always kept immersed in test tubes, containing paraffin surrounded by melting ice.

The voltage of the thermocouple was measured by a potentiometer of which a diagrammatic sketch (Fig. 2) is appended.

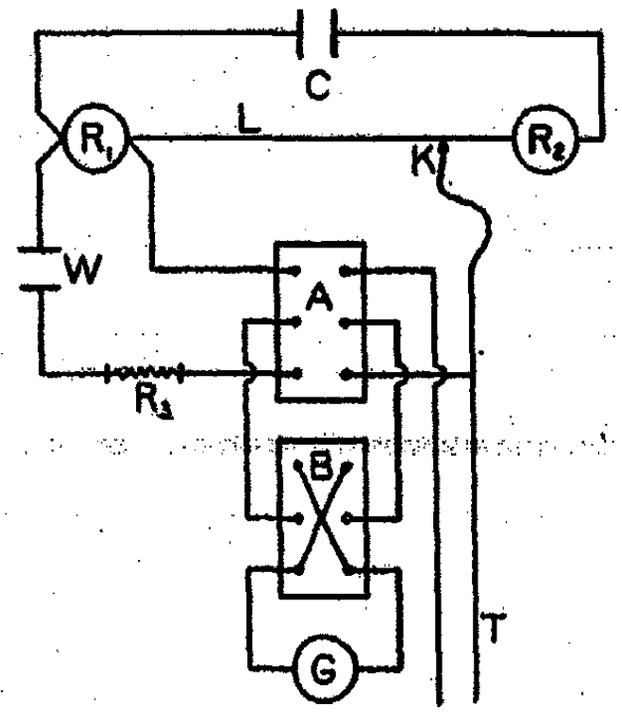


Fig. 2

C represents a small storage cell ($v = 2$), in whose circuit is included a resistance R_1 (1796.0 ohms), a wire of gilt manganin (resist. 18.780 ohms) and R_2 a variable resistance (about 1750 ohms).

The fall in potential along the wire L could readily be measured by means of the Weston standard cell. In the Weston circuit are included the known resistance R_1, a known length of the wire L, a connecting key K, the two switch boards A and B, and the galvanometer G. The resistance R_3 (a graphite resistance of 30000 ohms) could be inserted or short-circuited at will. The switch boards A and B were made with the usual mercury cups with reversible spiders.

By means of the spider A the Weston circuit or the thermocouple could be connected at will with the bridge wire, while the switch B served as a reversing key to the galvanometer.

The bridge wire consisted of two meters of gilt manganin wire of $^1/_{10}$ mm diameter, whose total resistance was 18.780

ohms. This wire was calibrated; but the correction curve varied so little from the normal that the additive correction could easily be neglected.

The standard resistance R_1 in the Weston circuit was accurately determined to be 1796.0 ohms.

The galvanometer was made by winding 250 yards of SPG wire on an old frame; its resistance was approximately 30.7 ohms and its sensibility 5×10^{-7} ampere.

Calibration of the Thermocouple

The calibration of the thermocouple was made as follows

Weston balance = 93.92 cms of wire = 8.8 ohms.

Resistance in Weston circuit 1796 + 8.8 = 1804.8 ohms.

Fall of potential along the wire per ohm of wire $= \frac{1.019}{1704.8}$.

1. Thermocouple Junction in Carbon Dioxide and Alcohol

Balance = 64.02 cms of wire

Resistance 6.096 ohms.

Voltage of thermocouple $\frac{1.019}{1804.8} \times 6.096 = 3441.8 \times 10^{-6}$ volts.

2. Thermocouple in Liquid Air

	Pressure on oxygen manometer mms	Temperature C	Weston balance cm	Voltage $\times 10^{-6}$
a	395	— 188.6	130.65	6922.6
b	480	— 186.9	129.75	6882.5

It is apparent that the voltage does not increase proportionally with the difference of temperature but increases more slowly as we descend the scale. If now we represent the relation between voltage and temperature by the equation

$$v = \alpha t - \beta t^2$$

where α and β are constants we find on substituting the above values for v.

$$\alpha = 49.5476 \times 10^{-6}$$
$$\beta = 0.60912 \times 10^{-6}$$

Now to prove whether this formula would serve for interpolation, I determined the temperature on the thermocouple scale of a mush of frozen ether, the temperature of which was also found simultaneously on an ethylene thermometer inserted in the mush.

3. Thermocouple in Frozen Ether.

Balance = 94.63 cms = 8.911 ohms.

$$\text{Voltage} = \frac{1.019 \times 8.911}{1804.8} = 5031.2 \times 10^{-6} \text{ volts}$$

Now substituting in the above equation

$$v = \alpha t - \beta t^2$$

we get $t = -121.7°$ C.

But the pressure on the ethylene thermometer was 222 mms.

Therefore the temperature was —121.7° C. (vide appendix II). It will thus be seen that the agreement between the temperature denoted by the thermocouple and by the ethylene thermometer is exact.

The equation $v = \alpha t - \beta t^2$ appears then to represent quite accurately the relation between the voltage of the thermocouple and temperature. For the particular thermocouple used the constants are

$$\alpha = 49.5476 \times 10^{-6}$$
$$\beta = 0.60912 \times 10^{-6}.$$

Apparatus

The apparatus used to determine the rise of boiling points of the solutions is illustrated in the accompanying diagram (Fig. 3).

The vessel D was made of thin glass about 10 cm in length and one cm in diameter. On the bottom of this tube was blown a vacuum vessel as in the figure.

During each experiment the outer vacuum vessel F was filled with liquid air to the level of the dotted line. The gas, then, which was introduced into the tube D, on coming into contact with the cold upper part condensed and collected

in the bottom of the tube. Here it was made to boil by means of a small bobbin of insulated copper wire N through which a small current could be sent by means of a single storage cell. The thermometer T was placed in the solution immediately over the ascending bubbles. Now as the vapor of the liquid rose in the inner vessel, it again came in contact with the cold upper part I of the tube, was again condensed and ran down to the liquid below. We thus have an apparatus work-

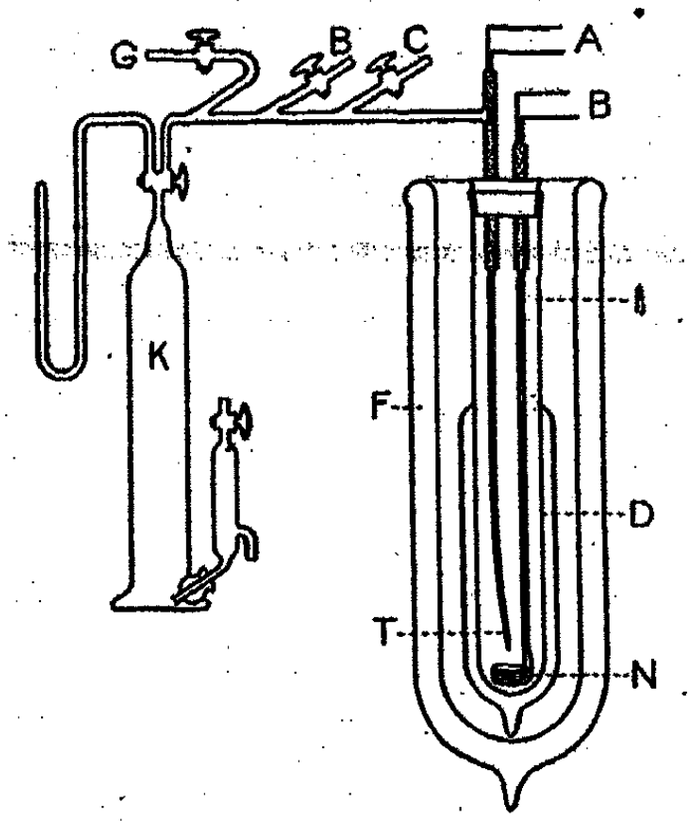


Fig. 3

ing as a reflux condenser at the temperature of liquid air. The gas cylinder served as a means of introducing the small quantities of the solute. The side tube G was connected through soda lime and phosphorus pentoxide tubes to a large gas cylinder containing the solvent to be used.

The tap B served as a pump connection and the tap C led to a mercury monometer by means of which the pressure of the vapor in the apparatus could be measured. The wires of the thermocouple and of the heating coil were led through small glass tubes and made gas tight by Chatterton cement.

Methods of Work

The method of experimentation was as follows:

After the apparatus had been thoroughly evacuated and found to be perfectly gas tight, a known volume (about two liters) of the pure solvent (say oxygen) was admitted through G and condensed in the tube D by means of the liquid air in the surrounding vacuum vessel. The stop cock at G was then closed and a small current was sent through the bobbin N. Almost immediately the liquefied gas began to boil steadily in D. As the condensation of the vapor continued, the liquid air in the outer vessel evaporated slowly and the temperature of the liquid in D also rose slowly.

A series of readings of temperature and pressure could thus be obtained readily and a part of the vapor pressure curve of the pure solvent could be plotted. The curve could again be easily retraced by placing more liquid air in the outer vessel, when, with the correspondingly greater surface of condensation more of the vapor in the inner tube was condensed and the temperature of the liquid accordingly fell. In this way the trend of the curve could be verified by successive observations.

When the vapor pressure curve of the solvent had been thus determined, the liquid air in F was removed, the tap G again opened, and the solvent allowed to evaporate back again into the gas cylinder from which it came.

The apparatus was then again evacuated. By means of the gas cylinder K, the solute was next introduced into the apparatus and carefully condensed in a solid ring at I just above the level of the evacuated part of E. A known volume of the solvent to be used was then introduced and condensed as before. By this means the solidified solute was continually washed by the descending streams of the liquefied solvent. The solubility of the substances used could thus be easily detected. If no solid remained at I the gases were completely soluble in one another.

The solution was then made to boil as before; temperature and pressure readings were taken from time to time, and the curve for the vapor pressure of the solution was plotted. From

the two curves thus obtained (the vapor pressure curves of solvent and solution) the value of $d'T$ could be directly obtained.

To illustrate the method, the curves for the vapor pressure of pure oxygen and of a mixture of oxygen and ethane are shown in the accompanying diagram. (Fig. 4)

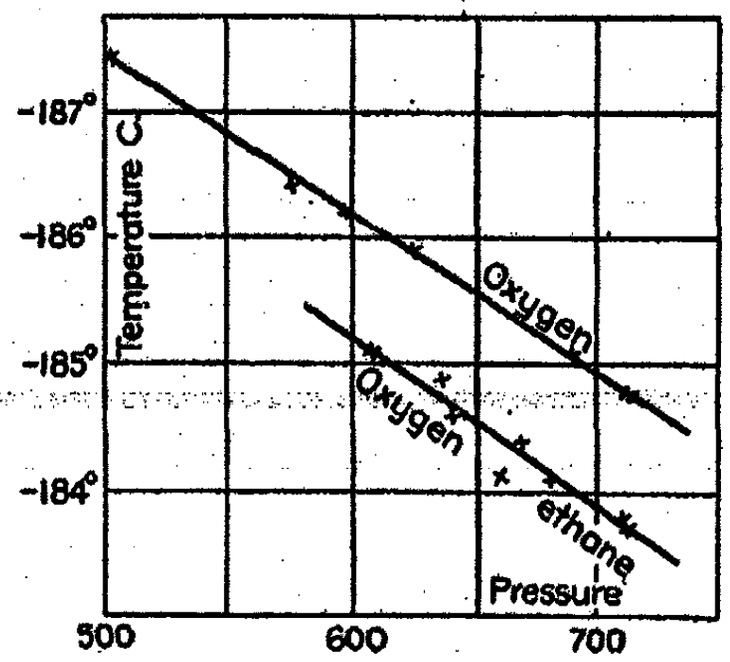


Fig. 4

The results obtained from the solution of all the commoner gases in oxygen and in methane are appended.

The calculated values for $d'T$ were obtained from the equation given on page 338. The temperatures corresponding to the pressures are given in each case on the centigrade scale.

Ethane appeared to be readily soluble in liquefied oxygen. Ethylene on the other hand, showed only a partial solubility. When the concentration of ethylene in oxygen rose to more than 1.9 percent solid ethylene could be seen floating in the liquid, but readily disappeared when more oxygen was condensed into the apparatus.

In addition to these two gases experiments were performed with nitrogen monoxide, acetylene; sulphur dioxide, nitrogen dioxide and nitrogen trioxide.

None of them appeared to show any solubility at all. The ring of solid remained throughout the experiment, and no change could be observed in the vapor pressure curve of the solution. If these gases are soluble at all, their solubility must be at any rate less than one percent.

SOLVENT OXYGEN

Solute	Percent conc.	From smoothed V. P. curves			dT	
		Press	t Solvent	t Solute	Obs.	Calc.
Ethane	6.5	600	184.7	184.05	0.65	
		650	183.75	183.2	0.55	0.59
		700	183.0	182.5	0.50	
	10.6	600	186.2	185.3	0.9	
		650	185.6	184.6	1.0	0.99
		700	185.0	183.95	1.05	
Ethylene	1.5	450	187.2	186.6	0.6	
		500	186.4	185.9	0.5	0.15
		550	185.6	185.1	0.5	
		600	185.0	184.5	0.5	
	1.45	550	185.3	184.9	0.40	
		600	184.65	184.25	0.40	0.14
		650	183.95	183.55	0.40	
		700	183.3	182.85	0.45	
	1.9	550	185.5	185.0	0.50	
		600	184.8	184.3	0.50	0.17
		650	184.15	183.65	0.50	
		700	183.5	182.95	0.55	

In the case of the two latter gases, nitrogen dioxide and nitrogen trioxide, the experiments were performed successively on the same mass of gas. The dioxide was first introduced and condensed as a white solid. After the solubility of the dioxide had thus been tried, the apparatus was allowed to warm up slowly. Soon after the dioxide began to melt, the white solid suddenly changed to blue. At this point the whole of the oxygen was again recondensed and the vapor pressure curve of the mixture was observed. The blue trioxide, however, showed no solubility in the liquefied oxygen.

Thus of the seven common gases which were tried, two only dissolved when oxygen was used as the dissolving substance.

We are thus left with only two series of results from which to argue as to the molecular aggregation of the gases concerned, and even in these two series we see quite a want of uniformity.

Ethane appears to dissolve in oxygen to any extent and to affect the boiling point quite in a normal way. We can thus conclude that ethane and oxygen retain the same relative molecular aggregation in the liquid and gaseous states.

But the ethylene dissolves in oxygen to the extent of 1.9% and raises the boiling point to a value which is approximately three times greater than the calculated rise. If this result be correct, then, we are driven to conclude either, that the molecules of ethylene are dissociating into three, or that three molecules of oxygen are agglomerating to form a single molecule in the solution. The former conclusion is, however, quite untenable according to our present views. We must, therefore, accept the latter view that the molecules of oxygen agglomerate in threes when ethylene is added to the solution. It need not necessarily follow, however, that oxygen always exists in trimolecular aggregates in the liquefied state.

But the number of the series of experiments performed is too small to allow of a perfectly definite statement of this association. And indeed it is difficult to see how the number can be augmented unless still more refined methods of measuring temperature changes produced by solubilities of less than one percent, can be introduced. This consummation would be difficult to obtain at the temperature of liquid air.

The next solvent tried was methane. The results are appended.

Both ethane and ethylene again appear to dissolve in all proportions in liquid methane.

The following gases were also tried: carbon dioxide, sulphuretted hydrogen, nitrogen monoxide, phosphoretted hydrogen, acetylene and sulphur dioxide. No trace of solution could be detected in any of these experiments, and in all cases the vapor pressure curves of the pure solvent and of the mixture were superimposed.

We are again left with two series of results from which to draw conclusions as to the molecular aggregation of gases dissolved in methane.

SOLID METHANE

Solute	Percent conc.	From smooth curve			dT	
		Press	t Solvent	t Solute	Obs.	Calc.
Ethane	7.7	225	176.1	175	1.1	
		250	175.2	174.1	1.1	0.75
		275	174.2	173.2	1.0	
	15.2	325	173.25	171.5	1.7	
		350	172.65	170.9	1.75	1.47
		375	172.05	170.3	1.75	
		400	171.5	169.7	1.8	
Ethylene	1.6	300	173.8	173.6	0.2	
		350	172.3	172.1	0.2	0.16
		375	171.5	171.3	0.2	
	5.8	225	176.05	175.4	0.50	
		250	175.15	174.6	0.55	0.58
		275	174.30	173 7	0.60	
	9.7	175	177.9	177.0	0.90	
		200	177.0	176.1	0.90	0.90
		250	175.2	174.4	0.80	

If first we take methane and ethylene, the rise of boiling point is normal; we therefore must conclude that these two gases retain the same relative proportion so far as their molecules are concerned in the liquid and gaseous states.

But when we consider methane and ethane we find that the observed value for the rise of boiling point is greater than the calculated value. Now we have again two reasons for this divergence:

(*a*) The dissociation of the ethane molecule,

(*b*) The association of the methane molecule.

If the former be true, we have in the first series a dissociation of 50 percent; in the second a dissociation of 20 percent of the total number of ethane molecules present. If the latter be correct, then we again have the quite unusual result that the association of the methane molecules is affected by the amount of ethane in the solution.

Now according to our present views we cannot conceive of the molecule C_2H_6 splitting up into simpler molecules of the

formula CH_3; we must then, as in the case of oxygen and ethylene, accept the latter conclusion that the presence of ethane produces an association of the molecules of methane, which increases as the percentage of ethane is increased.

Conclusions

The general conclusions of this research on the complexity of the molecules of gases in the liquid state may be briefly set forth as follows:

1. Oxygen and ethane retain the same molecular complexity in the gaseous liquid states.

2. Methane and ethylene also retain the same molecular complexity.

3. The presence of ethylene in oxygen and of ethane in methane produces an association of the molecules of the solvent: in the former case three molecules of oxygen, in the latter, two molecules of methane associate to produce a single molecule of the respective gases.

As regards the solubility of gases in one another we have the following results:

1. Ethane is soluble in oxygen in all proportions up to 15 percent.

2. Ethane is soluble in methane to the extent of at least 10 percent.

3. Ethylene is soluble in oxygen to the extent of 1.9 percent.

4. All the other commoner gases, carbon dioxide, sulphuretted hydrogen, acetylene, nitrous oxide, nitric oxide, phosphoretted hydrogen and sulphur dioxide are not soluble in oxygen or methane even to the extent of one percent.

APPENDIX

During the progress of the work the vapor pressure curves of the commoner gases were often required for thermometric measurements. The vapor pressure curves were accordingly ascertained by experiment, corresponding values for temperature and pressure being obtained by the platinum thermometer or the thermocouple and a mercury manometer respectively.

1. Methane

Liquid phase. The temperatures corresponding to different pressures in the liquid phase were determined by the thermocouple in the apparatus already described (Fig. 3).

The following values were obtained

Temp. abs.	Pressure in mms.
96.3	197
97.2	218
97.6	233
98.6	261
99.4	286
109.2	696
109.8	738

Now if we proceed according to the method of Ramsay and Young[1] to plot the ratio of the absolute temperatures of methane and water at the same pressure against the absolute temperature of water we find that these points lie fairly approximately on a straight line. This is shown in the accompanying diagram (Fig. 5).

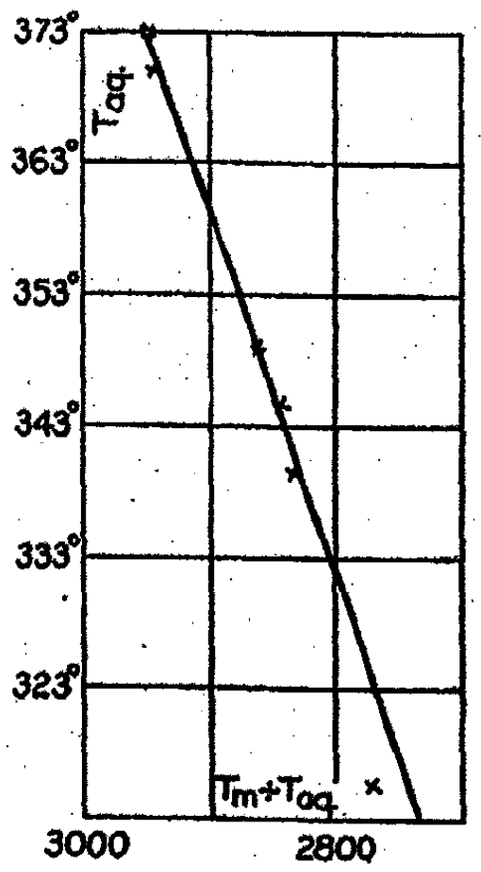


Fig. 5

[1] Phil. Mag., 21, 33 (1886).

From the vapor pressure curves of methane and water, we take the following values:

p	Tm	Taq	$\frac{Tm}{Taq}$
64	97.4	315.5	0.2769
200	96.4	339.5	0.2839
250	98.2	344.6	0.2849
300	99.9	348.9	0.2863
686	109.2	370.2	0.2949
738	109.8	372.2	0.2950

where Tm and Taq represent the temperatures of methane and water respectively at pressure p and $\frac{Tm}{Taq}$ the ratio of the same. The lowest point at a pressure 64 mm of mercury representing a point in the solid phase of methane falls off the straight line.

The results of this determination may therefore be considered as correct.

Values from the smoothed curve for methane were substituted in Biot's equation

$$\log p = a + b\alpha^t + c\beta^t$$

from which the values of the constants were found

$$a = 2.639 \qquad \alpha = 1.34643$$
$$b = 0.11239 \qquad \beta = 0.68896$$
$$c = -0.058998$$

From this the values of pressure corresponding to various temperatures in the liquid phase can be obtained.

Solid phase.—A bulb containing methane and connected with a mercury manometer was immersed in liquid air. The temperature of the liquid air bath could be varied by pumping off the air by means of a vacuum pump. The rapid evaporation produced a constant reduction of temperature. The liquid air can be made to boil quite smoothly by placing some cotton wool in the bottom of the vacuum vessel.

Applying smoothed values from this curve with the equation

$$\log p = a + b\alpha^t$$

we get

$$a = 1.3425$$
$$\log b = 0.01767$$
$$\log \alpha = 0.82113$$

From these equations for the solid and liquid phases we obtain the following results.

Solid phase		Liquid phase			
T (Abs)	Press	T	Press	T	Press
—	—	92	106	—	—
80	15	94	145	108	627
82	26	96	190	110	750
84	38	98	242	111	823
86	52	100	300		
88	68	102	365		
90	87	104	439		
92	108	106	525		

Freezing point.—Values above 88 mm on the solid curve and below 96 mm on the liquid curve have been determined by extrapolation. From the cutting of these curves the freezing point would be about 92° absolute and the melting pressure 107 mm.

But in several successive determinations the melting pressure of methane was found to be 92 mm.

This pressure on solid curve = 90.5
on liquid curve = 91.2

The freezing point would then lie between 90.5 and 91.2 Abs.

Boiling point.—From the liquid curve
the boiling point at 760 mm pressure = 110.2 Abs.
Olszewski[1] found 108.3
Ramsay and Travers[2] 112.7

[1] Comptes rendus, 100, 940.
[2] Travers : "Study of Gases," p. 243.

II. Vapor-Pressure of Ethylene

A small bulb containing ethylene was introduced into a bath of frozen ether. The pressure of the ethylene was taken by a mercury manometer; the temperature of the bath by the platinum resistance thermometer page (340).

Ethylene remains liquid throughout its range. At its melting-point it has no appreciable vapor-pressure.

The values of the V. P. curve are as follows:

Press	Temp: (Abs)	Olszewski
200	150	151.9
300	155.8	157.0
400	160.0	160.8
500	164.1	164.1
600	166.3	166.8
700	168.8	169.2
750	170.5	—
760	170.7	170.5
800	171.7	—

Boiling-point, 170.7 abs.

Other experimenters have found:

Olszewski,[1]	170.5
Ramsay and Travers,[2]	170.5
Wroblewski,[3]	169.5
Witkowski,[4]	169.5

III. Vapor-Pressure of Nitrogen Monoxide

Again a bath of frozen ether was used to maintain an approximate constancy of temperature. (To maintain this it was found necessary to surround the ordinary vacuum vessel containing the frozen ether with another containing animal wool saturated with liquid air.)

[1] Comptes rendus, 99, 133.
[2] "Study of Gases." p. 343.
[3] Wien. Akad., 1888.
[4] Phil. Mag., 1896, I.

The values obtained were as follows:

Press	T	Press	T
61	152	550	182.4
—	—	600	183.1
100	151.9	650	183.7
150	167.6	660	183.9
200	170.9	670	184.0
250	174.4	700	184.6
300	175.5	750	185.7
350	177.5	760	186.0
400	179.4	800	186.6
450	180.7	—	—
500	181.7	—	—

The melting pressure of N_2O was found to be 660 mm. This corresponds on both liquid and solid curves to the temperature 183.9 absolute.

Freezing-point = 183.9
Boiling-point = 186.0

Ramsay and Shields[1] using a hydrogen thermometer, found
Melting-point = 170.3
Boiling-point = 183.2

IV. Vapor Pressure of Acetylene

The bath used for maintaining a slow rise of temperature was frozen ether. The values for the curve above a pressure of 650 mm were obtained by extrapolation, as only a small quantity of pure acetylene was available for the determination.

Acetylene maintains the solid phase throughout.

Its melting-point lies above its boiling-point at the normal pressure of 760 mm.

Press	T.	Press	T.
70	161.0	450	188.0
100	164.9	500	190.3
150	169.7	550	192.4
200	174.3	600	194.2
250	177.6	650	195.8
300	180.3	700	197.2
350	182.8	750	198.7
400	185.6	760	199.0

[1] Jour. Chem. Soc., 63, 135 (1893).

The boiling-point determined by extrapolation is thus 199.0 absolute.

Travers' "Study of Gases" gives (without quoting the authority) the value 190.5.

V. The Solution of Ozone in Oxygen

In continuation of the work submitted in the previous paper I endeavored to dissolve ozone in oxygen with a view to determining the molecular weight of the former substance.

The apparatus used was similar in construction to that already detailed in the previous paper.

Oxygen made from potassium permanganate was dried over soda lime and phosphorus pentoxide—was then subjected to a silent electrical discharge and condensed in the small vacuum tubes used in the other experiments. From time to time during the ozonizing process, samples of the ozonized oxygen were drawn off through a solution of potassium iodide and the amount of ozone ascertained from the amount of iodine liberated by means of sodium thiosulphate.

When enough of the liquid solution had collected in the condensing vessel, it was made to boil by passing a small current through the copper coil immersed in the solution. The vapor pressure of the solution was then taken, the results plotted on a curve and compared with the vapor pressure of pure oxygen.

At the conclusion of the experiment, to prevent the explosion of the liquid ozone, when all the more volatile oxygen had evaporated, the liquid was blown out through a small capillary tube which passed through the cork to the bottom of the vessel. Fractionation of the solution was thereby avoided.

The temperature of the solution was first recorded by means of the iron constantan junction used in the previous experiments, but the thermocouple on these occasions failed to give consistent results. The only reason that can be assigned for this is that the presence of the ozone had oxidized the junction of the metals throughout and destroyed the utility of the thermocouple.

I therefore constructed a small platinum thermometer and determined its resistance in the usual way on a Callendar recorder. From this resistance the temperature was readily obtained. The constants of the thermometer, previous to its being sealed into the apparatus, were determined to be as follows:

Resistance in ice	5.339
in steam	7.182 ohms (t 100.1)
Absolute zero	290.0
Resistance in liquid air	1.722
(t = 183.7 on oxygen therm.)	
Temp. on pt scale	196.8

$\therefore \delta$ from the equation $t - pt = \delta\left(\frac{t}{100} - 1\right)\frac{t}{100} = 2.45$

When, therefore, we know pt from the observed resistance we can calculate the value of t from this equation.

The concentration of the ozone in solution could be readily varied in the experiments. By running in the oxygen at the rate of about 6 liters in one half an hour, a concentration of about 5 percent of ozone could easily be obtained.

Smaller concentrations were produced by ozonizing only part of the ingoing gas. Higher concentrations were obtained by boiling off part of the oxygen from the solution and then condensing more ozonized oxygen to take the place of the oxygen removed. By this means a concentration of about 8 percent was obtained.

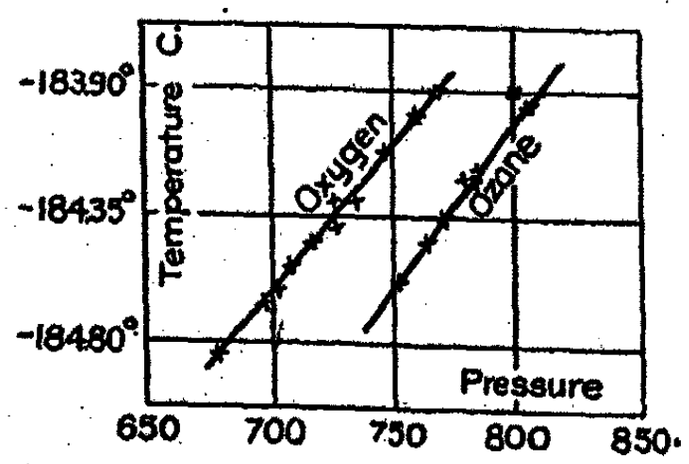


Fig. 6

The curves for concentrations of 4 and 5 percent are appended—in the experiments on solutions in which the concentra-

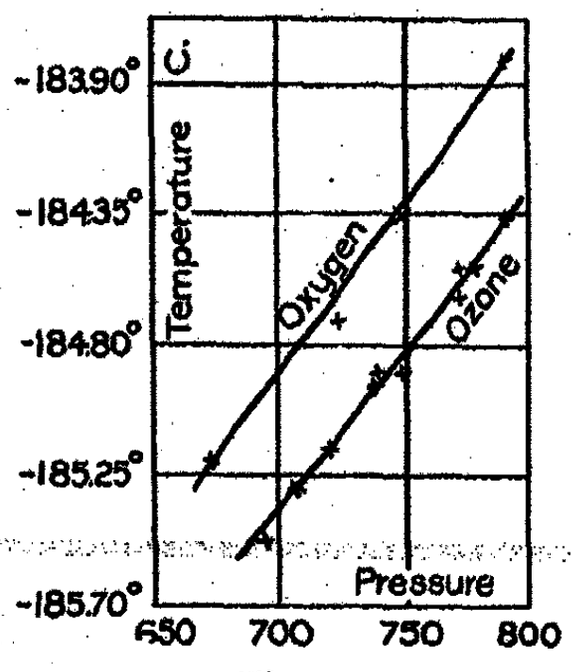


Fig. 7

tions were respectively 2, 6.5 and 7.5 percent, the curves are almost coincident with one another.

The final results of the five experiments performed are tabulated as follows:

Percent concent. of ozone	Rise of boiling-point of solution	Absolute boiling-point
nil	—	90.2
2	−0.05	90.15
4	−0.50	89.70
5	−0.45	89.75
6.5	+0.25	90.25
7.5	+0.17	90.37

Now if we plot these values of concentration against the change in boiling point of the solution we find that they fall approximately on a curve over the small range in which the experiments were made. This curve moreover changes its direction between concentrations of 4 and 5 percent.

This point then appears to represent a constant boiling mixture of oxygen and ozone of minimum boiling-point.

In view of this it was found that the molecular complexity of the ozone could not be determined by finding the rise

in boiling-point produced by dissolving known percentages of ozone in oxygen. The boiling point of the minimum boiling-point mixture appears to be about 89.7° absolute.

Nitrogen and Ozone

I next attempted to dissolve ozone in nitrogen. The apparatus was identical with that already described. Oxygen was first ozonized by a silent electric discharge and then condensed. The oxygen was then removed by evaporation and an attempt was made to introduce nitrogen previously cooled by passing through a spiral immersed in liquid air.

As the last traces of oxygen were removed, the ozone (which in all was equal to 300 cc of gas) exploded so violently that no part of the apparatus in the immediate vicinity remained. No trace indeed of the platinum thermometer was to be found.

Under such circumstances further attempts at finding a solvent for ozone were abandoned.

In conclusion I must render my thanks to Professor Ramsay for the interest he has taken in the progress of the work. I should like also to thank Professor M. W. Travers and Mr. N. T. M. Wilsmore for the assistance they have rendered me in the same.

University College, London, 1905.

THE ABSORPTION OF POTASSIUM BY SOILS[1]

BY OSWALD SCHREINER AND GEORGE H. FAILYER

For studying the absorption of potassium by soils a solution of potassium chloride containing 200 p. p. m. K was used. Three of the soils studied were the same as those used in the phosphate experiments, described in a former paper,[2] namely, the clay soil, the clay loam and the fine sandy soil. In addition to these, two other soils were studied, a loam and a sand.

The apparatus and general manipulations were the same as in the experiments with the phosphate absorption already described. The soil was not previously washed with water but was used in the air-dried state in which it had been kept for some weeks in the laboratory. The apparatus was filled with the solution as already described and regulated so as to have a flow of about 50 cubic centimeters in twenty-four hours. The concentration of the potassium in the percolates was determined colorimetrically.[3]

Absorption of Potassium from a Solution of Potassium Chloride

In Table I are given the results obtained with the clay soil. In the first column are given the total number of cubic centimeters of solution passed through the soil, in the second column the concentration in potassium of the successive fractions, and in the third column the total amount of potassium absorbed by the soil. The fourth column gives the calculated amount of absorbed potassium obtained by a formula which will be described later. It will be noticed from the results in the second column that the concentration of the first few hundred cubic centimeters of the 200 p. p. m. solution in passing

[1] Published by permission of the Secretary of Agriculture.

[2] Jour. Phys. Chem., 10, 239 (1906).

[3] Colorimetric, Turbidity, and Titration Methods, Potassium I, p. 31, Bull. 31, Bureau of Soils, U. S. Dept. of Agric., 1906.

through the soil was reduced to approximately 60 p. p. m. and that with succeeding fractions the concentration gradually rose, showing a tendency to reach the original concentration of the solution, until when about 1100 cc had passed it was 173 p. p. m. At this point the soil had absorbed nearly 900 p. p. m. of potassium.

TABLE I

Absorption of potassium by a clay soil from a solution of potassium chloride containing 200 p. p. m. K.

Total cc. of percolate	P. p. m. K in solution	Total p. p. m. K absorbed by soil	
		Observed	Calculated
50	62	70	—
160	57	230	230
210	57	300	300
260	60	370	370
320	78	440	440
410	104	520	530
500	117	600	610
550	117	640	640
610	133	690	690
690	141	740	730
750	156	760	760
890	165	810	820
970	164	860	850
1140	173	890	890

The absorption obtained with the clay loam is shown in Table II. The absorption of potassium by this soil is not so great as by the clay soil, nor is it so great as the absorption of phosphate by this same soil; nevertheless, the second column shows that the first fractions of the 200 p. p. m. solution are reduced to approximately one-half that concentration by passing through the soil. As more solution passes, the concentration rises and slowly approaches the original value, having risen to 180 p. p. m. when about 1400 cc of the solution have passed through the soil, which at this point has absorbed nearly 600 p. p. m. of potassium.

TABLE II

Absorption of potassium by a clay loam from a solution of potassium chloride containing 200 p. p. m. K.

Total cc. of percolate	P p. m. K in solution	Total p. p. m. K absorbed by soil	
		Observed	Calculated
50	101	50	—
100	99	100	100
350	125	290	270
500	167	340	340
680	164	400	410
880	167	470	470
1060	178	510	510
1240	175	550	540
1390	180	570	560

The absorption in the case of the loam was even more marked than with the clay loam, though less than with the clay soil. The first fraction was higher than the four succeeding ones and is doubtless owing to the same causes which produced the higher concentrations in the first fractions of the percolate obtained in the disodium phosphate experiments. This higher concentration of the first fraction is noticed also with the two soils already described, although not so marked, and is also shown with the other soils. The solution was reduced to approximately 70 p. p. m. after which the concentration again rose until when about 700 cc had passed through the soil it was 150 p. p. m. The experiment was not continued beyond this point.

The absorption by the fine sandy loam was much less than by the soils so far described, but it was nevertheless quite marked in the first fractions of the solution passing through the soil (about 100 p. p. m.) The absorption by the sandy soil was still less in amount but definitely traceable in the various portions of percolate.

Removal of Absorbed Potassium by Water

The removal of the absorbed potassium from the two soils was also studied, the soils used being the clay soil and the clay

loam of the previous experiment. For this purpose the well-drained soils, containing 890 and 570 p. p. m. of absorbed potassium, respectively, were washed by filling the apparatus with distilled water and continuing the percolation at the same slow and constant rate used in passing the potassium chloride solution. The percolate, collected in fractions, was analyzed for potassium as before. The results for the clay soil are given in Table III. The quite high concentration of the small fraction collected at the start is owing to the stronger solution contained in the soil. On passing more water the percolate becomes rapidly weaker in potassium until when about 450 cc have passed, the concentration shows a practically constant composition of about 20 p. p. m., although the percolation was continued until over 2000 cubic centimeters had been passed and

TABLE III

Removal of absorbed potassium from a clay soil by water

Total cc. of percolate	P. p. m. K in solution	Total p. p. m. K remaining in soil
—	—	890
40	171	820
80	78	790
130	56	770
170	47	740
220	45	720
310	29	700
450	21	670
520	19	650
720	20	610
780	19	600
840	19	590
1150	22	540
1260	20	520
1370	19	500
1510	21	470
1640	19	440
1760	19	420
1870	17	400
2110	19	360

the concentration of absorbed potassium in the soil was reduced from 890 p. p. m. to 360 p. p. m.

The removal of the absorbed potassium from the clay loam is shown in Table IV. The results in this case are very similar to those of the clay soil, although the washing with

TABLE IV

Removal of absorbed potassium from a clay loam by water

Total cc. of percolate	P. p. m. K in solution	Total p. p. m. K remaining in soil
—	—	570
70	89	510
140	59	470
200	43	440
330	31	400
470	30	360
660	30	310
720	28	290
780	30	270
830	26	260
880	25	250

water was not continued so long. The concentration of the solution is higher, showing the more ready removal of the potassium from this soil. When 880 cc of water had passed through the soil the concentration was 25 p. p. m. and the amount in the soil had been reduced from 570 to 250, whereas in the case of the clay soil the passage of a similar amount of water had reduced the soil from 890 to only about 600 and the concentration of the percolate had dropped down to the constant concentration of approximately 20 p. p. m.

Graphical Representation and Discussion of the Results

In the following figures are given the curves for the results obtained in the experiments on the absorption of potassium as well as those obtained in the removal of the absorbed potassium by water. In Figure 1, are shown the results obtained with the solution. The abscissas represent the volume of the solution or of water which has passed through the soil

and the ordinates the concentration of potassium in the percolate. The upper boundary line of the figure gives the strength of the solution before passing through the soil; and the break in the curves shows the point where the solution was replaced by distilled water and the removal of the absorbed potassium begun. The results for the clay and clay loam only are given in

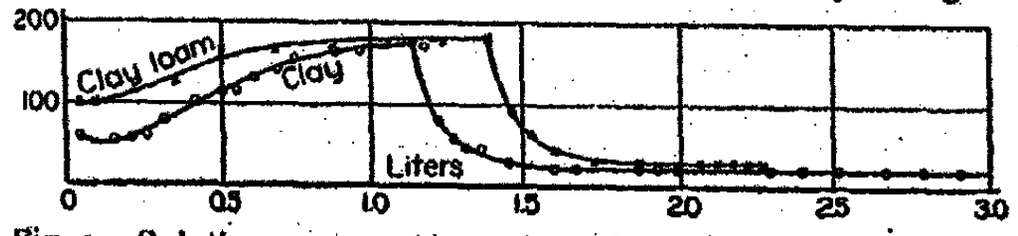


Fig. 1. Solution curves. Absorption of potassium by soils from a solution of potassium chloride and the removal of the absorbed potassium by water.

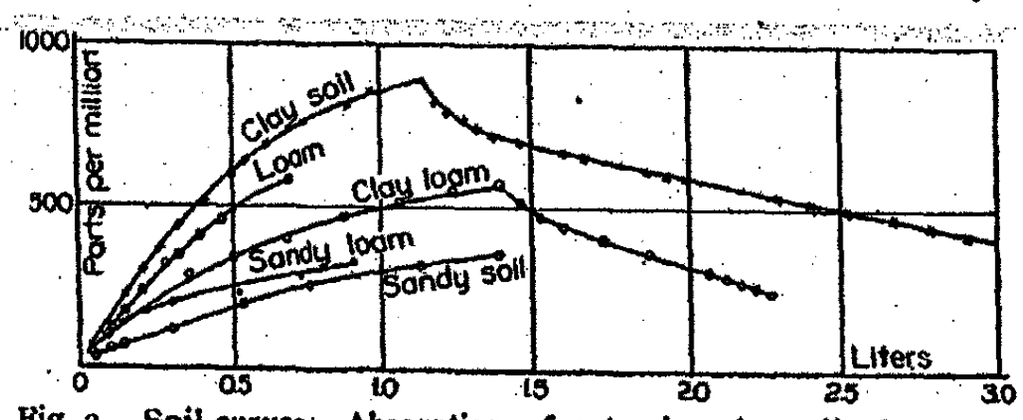


Fig. 2. Soil curves. Absorption of potassium by soils from a solution of potassium chloride and the removal of the absorbed potassium by water.

this figure, as these are the two soils in which both the absorption and removal of potassium was studied. The absorption curve for the loam would lie between those of the clay and clay loam, the curves for the sandy loam and sand would lie above that of the clay loam. It is apparent from the figure that the general run of the absorption and removal of the potassium is very similar to the phosphate curves given in the preceding paper. The curves show very strikingly that the concentration of the first few hundred cubic centimeters of the solution is materially reduced, in the one case approximately to one-half and in the other to one-fourth the original strength. With increase in the volume of percolate the curves rise slowly, and approach the upper boundary line of the figure; that is, the ordinate of the original strength of the solution, apparently asymptotically. The removal of the absorbed potassium is

very rapid at first but the solutions soon reach a constant concentration as is very strikingly shown by the horizontal position of the removal curve in both cases. A comparison with Figure 2, also shows that the concentration of the solution becomes constant at a point where only about one-third of the absorbed potassium has been removed. It is also noteworthy that the clay soil, although it contains throughout a much larger amount of absorbed potassium, gives a lower concentration of potassium in solution than does the clay loam with its lower potassium content. It follows therefore that the relative concentration of the potassium in the percolates gives no indication of the amount of absorbed potassium present in the soil, and it must be admitted that this is in a readily water-soluble form as is shown by the continued removal of potassium by water in the above experiments. The magnitude of these absorption results and the removal of the absorbed material shows that in experiments dealing with the solubility of finely powdered substances of slight solubility, such as soils or rock-forming minerals, it is not so much the solubility itself with which one is dealing as the absorption phenomena and the removal of the absorbed products. The results obtained by the removal of the absorbed potassium by water are even more striking than in the case of the phosphates and the conclusion that the concentration in the free soil moisture is dependent on the absorptive power of the soil is well supported by these results.

In Figure 2 are shown the results expressed in terms of the soil itself, the abscissas being the volumes of solution or water passed through the soil, and the ordinates the amounts of potassium absorbed by the soil. It is at once apparent that the different soils show marked differences in their absorptive power for potassium. The clay loam for instance, is approaching a saturated condition with a concentration of potassium in the soil at which the clay soil is still absorbing at a rapid rate. Similar differences are shown by the other soils in the amount of the absorption, but it is at once apparent

that the general run of the curves is the same as those of the more thoroughly studied clay soil and clay loam. The removal curves drop rapidly at first and then run downward in a straight line in the case of both of the soils studied. The similarity of the potassium absorption curves to those of the phosphate absorption curves given in the preceding paper, in that they tend to approach a horizontal asymptote, is striking. It has been found that these results are quite accurately described by the same differential equation which describes the phosphate absorption curves,

$$\frac{dy}{dv} = K(A - y)$$

or integrating

$$\log (A - y) = \log A - Kv$$

where K is a constant and A is the maximum amount of the potassium the soil can absorb under the conditions of the experiment, *i. e.*, the specific absorptive capacity of the soil for potassium; y is the amount of potassium the soil has absorbed when the volume v of solution has passed through the soil. In these experiments, however, as in the case of the disodium phosphate, it is necessary, on account of the fact that the curves do not pass through the origin, to substitute $\log (A - y_0)$ for log A, where y_0 is the ordinate of the point taken as the first reading, and also to substitute the value of $(v - v_0)$ for v, where v_0 is the volume corresponding to y_0 taken as the first reading. The equation then becomes

$$\log (A - y) = \log (A - y_0) - K (v - v_0).$$

The formula has been applied to the results obtained with the clay soil and clay loam. When the following values are used, a very good agreement is found between observed and calculated results.

	A	$\log (A - y_0)$	K
Clay soil.....	1000	2.886	0.000864
Clay loam.....	650	2.740	0.000622

The method of calculation was exactly the same as already described in the phosphate paper. In the fourth columns of the absorption results for the respective soils are given the calculated values. In Figure 2 the absorption curves for the clay soil and clay loam are drawn through the calculated points, the experimental points being indicated by the respective signs, and the curves show therefore how well the calculated and observed results agree.

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ON THE THEORY OF FLUORESCENCE[1]

BY GERTRUD WOKER

It is known that fluorescence and color may occur simultaneously in one and the same substance. This is usually the case when the following conditions are fulfilled:

(*a*) Absorption bands in the ultra-violet or in the visible part of the spectrum.

(*b*) Absorption bands in any part of the visible spectrum.

(*c*) Reflection of, or transparency to, part of the visible spectrum.

(*d*) Change of a part of the absorbed rays into those of the visible spectrum.

(*e*) Change of a part of the absorbed rays into heat.

The conditions (*a*) and (*d*) are essential to fluorescence and the others, (*b*), (*c*) and (*e*) to color. Even when all these are satisfied, it may happen however that a substance, though colored, does not fluoresce. An actual fluorescence may be masked by being identical with the color of the substance, as was pointed out by Richard Meyer[2]; it is also possible that an intense fluorescence may become invisible if it is complementary to the strong color of the substance itself or to a highly colored impurity. Thus an intense yellowish-orange color of the substance itself or of an impurity contained in it would nullify a blue or violet fluorescence.

I have actually observed that the bluish fluorescence of quinine sulphate disappears on adding a solution of picric acid and that methyl orange masks the fluorescence of petroleum. On dissolving more and more picric acid in petroleum the fluorescence becomes weaker and weaker, finally disappearing. The naphthoflavanone, recently prepared by me, shows a beautiful bluish fluorescence only when the perfectly pure

[1] Translated from the author's German manuscript by W. D. Bancroft.

[2] Zeit. phys. Chem., 24, 479 (1897).

product is dissolved in colorless ethyl alcohol. If the alcoholic solution is colored yellow by traces of chalkone, the fluorescence cannot be detected.

Over and above these observations, the following known facts illustrate the damaging effect of complementary colors. The violet fluorescence of pure chrysene is entirely masked by the yellow color of the impurity which it is so difficult to remove. The yellow solution of anthracene in sulphuric acid shows no trace of the blue anthracene fluorescence. The 3,2-diethoxy-flavone[1] dissolves in sulphuric acid at first with a yellow color. After standing awhile the solution becomes colorless. As the color disappears the clear blue fluorescence becomes visible and is at its best when so much sulphuric acid is added that the solution becomes colorless. In the xanthone group, which has been studied carefully in the laboratory of Berne University by v. Kostanecki and his students, the violet and blue fluorescence is visible only when the solution is colorless and disappears when the solution is even faintly yellow[2].

By adding a solution with a color complementary to that part of the substance in question it ought to be possible to develop fluorescence in a non-fluorescing derivative of a fluorescing, colored substance, or to increase an actual fluorescence. In the most favorable case the existence of color will have no effect on the fluorescence, while in the most unfavorable case it will obliterate the fluorescence. This last case is very conspicuous in the anthracene group where the color and the fluorescence each[3] kills the other. Between these two extremes are to be found all possible intermediate forms in which the fluorescence is more or less affected or displaced by the color. Just for this reason in many cases, the fluorescence of a compound will be much damaged by the presence of chromophoric groups, especially of complex chromophores

[1] v. Kostanecki and v. Salis: Ber. chem. Ges. Berlin, 32, 1020 (1899).

[2] The same thing can also be noticed in sulphuric acid solution.

[3] Liebermann: Ber. chem. Ges., Berlin, 13, 913 (1880). R. Meyer: Zeit. phys. Chem., 24, 468 (1897).

TABLE I

Oxyxanthones	Color in solution		Fluorescence	
	in alkalies	in H_2SO_4	in alkalies	in H_2SO_4
1-oxyxanthone[1]	yellow insoluble sodium salt	yellow	none	none
2- " [2]	yellow	"	"	faint green
3- " [2]	colorless	almost colorless	bluish	bluish
4- " [3]	yellow	yellow	none	none
1-3-dioxyxanthone[4]	"	—	"	—
1-6- " [5]	"	—	"	—
3-6- " [6]	" (faint)	—	intense violet	—
3-4- " [7]	red	—	none	—
2-8- " (euxanthone)[8]	yellow	—	"	—
1-3-7-trioxyxanthone (gentiseine)[9]	—	—	"	—
7-methyl-1-oxyxanthone[10]	—	intense yellow, weaker in very dilute solutions	—	very faint or none
5- " 1- " [10]	—	—	—	—
6- " 1- " [10]	—	—	none	none
7- " 3- " [10]	colorless	—	bluish	greenish-blue
5- " 3- " [10]	—	—	—	blue-green
6- " 3- " [10]	—	—	—	blue

[1] Michael: Am. Chem. Jour., 5, 95 (1884); Graebe: Liebig's Ann., 254, 289 (1889); v. Kostanecki and Nessler: Ber. chem. Ges. Berlin, 24, 1884 (1891).
[2] v. Kostanecki and Nessler: Ibid., 24, 1984 (1891).
[3] v. Kostanecki and Rütishaus: Ibid., 25, 1648 (1892).
[4] v. Kostanecki and Nessler: Ibid. Also Berne: Thesis.
[5] v. Kostanecki and Nessler: Ibid., 27, 1991 (1894).
[6] R. Meyer and Conzetti: Ibid., 30, 970 (1897).
[7] Graebe and Eichengrün: Ibid., 24, 969 (1891).
[8] Graebe: Liebig's Ann., 254, 265 (1889); v. Kostanecki: Ber. chem. Ges., Berlin, 24, 3983 (1891); v. Kostanecki and Nessler: Ibid., 27, 1989 (1894).
[9] Tambor: Berne thesis. v. Kostanecki and Tambor: Monatsheft, 12, 207 (1891); 15, 4 (1894).
[10] Berne thesis.

with intense colors. This can be seen most clearly by comparing the fluorescence of colored substances with those of the corresponding leuco-compounds.

Liebermann[1] has shown that neither anthraquinone nor its derivatives are fluorescent, while fluorescence is to be found in pure anthracene compounds in which the ketone group has been reduced. The fluorescence of the anthraquinones is checked by the intensely colored complex chromophore O :C . C . C :O. If this is more or less completely destroyed by the addition of hydrogen, the fluorescence phenomena of the anthracenes, anthranols and oxyanthranols appear, as described by Liebermann.[1] As a further example we may cite the diphenylquinoxaline with the complex chromophore[2] N :C . C :N. There is no fluorescence to this substance but there is to its leuco-compound, diphenyl-dihydroquinoxaline, in which one of the double bonds has been broken. By addition of phenol the diphenylquinoxaline can be converted into a fluorescing azonium base[3] which is probably due to the fact that the introduction of another phenyl group develops new ultra-violet absorption bands in the compound and to these is due the increased fluorescence.

The nitro group seems to be the most effective of all the chromophores in checking fluorescence.[4] It is quite possible that this peculiarity is connected with the fact that most nitro compounds are yellow. From the facts previously cited it appears that a yellow color in alkaline solution causes the violet and blue fluorescence of the xanthone compounds to disappear and that the bluish fluorescence of petroleum and of quinine sulphate solution can be nullified by addition of methyl orange or picric acid. The complementary nature of the two sets of colors is apparently the cause of the phenomenon.

[1] l. c.
[2] O. Fischer: Ber. chem. Ges., Berlin, 25, 2826 (1892); 27, 719 (1894).
[3] O. N. Witt: Ibid., 20, 1183 (1887).
[4] R. Meyer: Zeit. phys. Chem., 24, 482 (1897).

Since the blue to violet fluorescence is the most common type, it is quite conceivable that yellow is the color which is chiefly antagonistic to fluorescence. Among chromophores the most antagonistic would be those causing a yellow color, and therefore pre-eminently the nitro group.

The facts observed by Liebermann, O. Fischer and others justify us in concluding that the chromophore is the most important factor in the destruction of fluorescence in colored substances. The fluorescing leuco-compounds differ from the non-fluorescing dye-stuffs only in one thing—the absence of the chromophore. The chromophore is consequently the cause of the different behavior of the two classes of compounds. The chromophore causes the partial displacement of the absorbed rays from the ultra-violet to the visible spectrum, possibly also the appearance of new absorption bands, and it causes a reflection of part of the visible spectrum. This reflected part is the one which weakens or destroys the fluorescence when complementary to it. Great stress is also to be laid on the first point, on the displacement of the absorption bands from the ultra-violet to the visible spectrum, especially in chromophores with high refraction and dispersion constants. The greater the displacement towards the red end of the spectrum the less is the possibility of fluorescence. By heaping up chromophores, the absorption bands can be displaced into the ultra-red, and fluorescence becomes impossible. The chromophoric groups therefore work against fluorescence in two ways.

A different behavior is shown however by those compounds in which the absorption bands are far out in the ultra-violet and are only brought into the region of the visible spectrum by introduction of groups containing double bonds.

A solvent (Kundt) can also have something the effect of a chromophoric group and can displace an absorption band towards the red end of the spectrum, this displacement being greater the greater the dispersion of the solvent. This established relation between fluorescence and the dispersion of

the solvent throws some light on the action of chromophoric groups. The double bond, characteristic of the chromophores, causes a marked increase in the dispersion constant as compared with a single or a triple bond (Brühl). Since adjacent chromophores re-enforce each other, the heaping up of double bonds, so characteristic of complex chromophores, causes an enormous increase in the dispersion constants and also a marked displacement of the absorption bands towards the red end of the spectrum.

Increase of dispersion, the phenomenon of color, and the weakening of fluorescence appear in general all to be consequences of a special, presumably denser, form of matter such as we represent to ourselves by atomic groups with double bonds.

The fluorescence is affected markedly and in an unfavorable manner by the salt-forming groups[1] of the dye-stuffs as well as by the chromophores. This is intelligible because most of the salt-forming groups displace the absorption bands towards the red end of the spectrum (Schütze's bathochrome groups). Only a few, such as the amino group, cause a displacement of the absorption bands towards the violet end (Schütze's hypsochrome groups) and these increase the fluorescence when no other countervailing factors occur. The salt-forming groups are especially destructive of fluorescence when they have an auxochrome nature and re-enforce the dye-stuff. St. v. Kostanecki[2] has shown that the color of a compound is more intense, the nearer the salt-forming group is to the chromophore. Salt-forming group and chromophore re-enforce each other

[1] In the paper which I have already cited many times, R. Meyer called attention to the changes in the fluorescence of a compound caused by the introduction of an OH or NH_2 group. He showed that in the xanthone group substitution in positions 3 and 6 is favorable to fluorescence, especially when both are occupied by OH or NH_2, while substitution in position 1 has the opposite effect. Since Meyer says nothing about the possible causes of this isomerism phenomenon, I have considered the subject from a different point of view.

[2] Ber. chem. Ges., Berlin.

more, the nearer they are, the effect being similar to but not so marked as that of two chromophores. Two adjacent hydroxyl groups re-enforce each other in a like manner as is shown by observations on xanthones, flavones and dioxyanthraquinones.

Just as with the chromophores, this re-enforcement usually weakens the fluorescence in two ways. First, as has already been said, because of an increase in the color which makes the fluorescence less visible and especially when the color and the fluorescence are complementary. Second, because the re-enforcement of the chromophore by the salt-forming group or the mutual re-enforcement of two adjacent hydroxyl groups causes an increased displacement of the absorption bands towards the red end of the spectrum, thus decreasing the possibility of fluorescence.[1]

In agreement with our theoretical predictions we see in Table I that all the xanthones, having hydroxyl groups next a carbonyl group, or two free hydroxyl groups in the ortho position show either no fluorescence or a very slight one visible only at great dilutions. The fluorescence becomes more intense the farther the hydroxyl is from the carbonyl group. In 2-oxyxanthone there is a slight fluorescence in sulphuric acid solution. In 3-oxyxanthone the fluorescence is stronger and is visible both in alkaline and in sulphuric acid solution. The maximum is reached not when one para position to the carbonyl group is occupied but when both are. With the oxyxanthones and oxyphenonaphthoxanthones the variation of the fluorescence with the position of the hydroxyl group can be used for determining the constitution.

With the flavones we observe the same thing as with the xanthones, though here the often greenish fluorescence is less affected by the natural color of the solution than is the case with

[1] In these cases, as in the previously considered case of the chromophores, there is the same limitation and possible reversal of the principle for the case of absorption bands far out in the ultra-violet.

the bluish fluorescence of the xanthones. Among the monoxyflavones the 3-oxyflavone,[1] with the hydroxyl in the para position to the carbonyl group, has a beautiful bluish fluorescence in an almost colorless solution. The 2-oxyflavone,[2] on the other hand, has only a faint green fluorescence while the 1-oxyflavone, which has not yet been made, will probably not fluoresce. This conclusion is justified by the similarity between the xanthones and the flavones and by the behavior of the polyoxyflavones which contain a hydroxyl adjacent to the carbonyl group and which all show very slight fluorescence in comparison with their isomers. Thus, among the dioxyflavones, chrysene[3] (1-3-dioxyflavone) has no fluorescence, in marked contrast to its isomers with the exception of 3-4-dioxyflavone.

Specially noticeable for marked fluorescence are those derivatives which have a hydroxyl in the para position to the carbonyl group. These are the 3.2′-dioxyflavone,[4] and the 3.3′-dioxyflavone[5] and the 3.4′-dioxy flavone,[6] all of which show a blue fluorescence. If a hydroxyl group be introduced into these compounds in the ortho position to the carbonyl group, we have the following substances: 1.3.2′-trioxyflavone;[7] 1.3.3′-trioxyflavone;[8] and 1.3.4′-trioxyflavone[9] (apigenine). Apigenine and the 1.3.2′-trioxyflavone have only a faint greenish fluorescence while the 1.3.3′-trioxyflavone does not fluoresce at all. Two free hydroxyls in adjacent position have a weakening effect on fluorescence similar to that of the ortho position of hydroxyl and carbonyl groups. Like the 3.4-dioxyxanthone,

[1] St. v. Kostanecki and Emilewicz: Ber. chem. Ges., Berlin, 31, 699 (1898).
[2] St. v. Kostanecki, Tambor and Levi: Ibid., 32, 326 (1899).
[3] St. v. Kostanecki, Tambor and Emilewicz: Ibid , 32, 2448 (1899).
[4] St. v. Kostanecki and v. Salis: Ibid., 32, 1030 (1899).
[5] St. v. Kostanecki and v. Harpe: Ibid., 33, 322 (1900).
[6] St. v. Kostanecki and Osius: Ibid., 32, 321 (1899).
[7] St. v. Kostanecki and Webel: Ibid., 34, 1454 (1901).
[8] St. v. Kostanecki and Steuerman: Ibid., 34, 109 (1901).
[9] St. v. Kostanecki, Tambor and Czajkowski: Ibid., 33, 1988 (1900).

which is red in alkali solution, the 3.4-dioxyflavone[1] does not fluoresce.

The 2.3′-dioxyflavone[2] fluoresces green and changes into the non-fluorescent 2.3′.4′-trioxyflavone[3] when a hydroxyl is introduced in the position 4′. A similar behavior is to be noticed with the 3.3′-dioxyflavone[4] which has a beautiful blue fluorescence and with the 3.4′-dioxyflavone[4] which has a violet fluorescence. Both change into the 3.3′.4′-trioxyflavone[5] which shows only a faint green fluorescence.

Lastly, it is to be noticed that luteoline,[6] which does not fluoresce, has two adjacent hydroxyl groups in addition to the hydroxyl near the carbonyl group. There are therefore two factors in this case tending to decrease the fluorescencee

This is the place to mention an experiment which shows the bad effect of two adjacent ortho groups upon fluorescence. On subjecting resorcinol to the zinc chloride fusion I obtained a substance which fluoresced as powerfully as fluoresceine itself. On condensing pyrogallol in the same way a substanc. was found which did not fluoresce at all. That at least a pair of free adjacent hydroxyls remained intact in this substance is shown by its character as a dye-stuff. With cotton mordanted with metallic oxides (Scheurer strips), with wool and with silk it produced a grayish green color, quite different from that which pyogallol itself causes.[7]

Very often the regularities may be upset by a hydroxyl group reacting with a neighboring phenyl group forming a nearly closed new ring system which, in many cases, has the same marked tendency to fluoresce as a completely closed system. It is well known that the closing of the ring

[1] St. v. Kostanecki, Tambor and G. Woker: Ibid., 36, 4235 (1903).
[2] St. v. Kostanecki and Blumstein: Ibid., 33, 1478 (1900).
[3] St. v. Kostanecki and Schmitt: Ibid., 33, 327 (1900).
[4] l. c.
[5] St. v. Kostanecki and Rozycki: Ibid., 34, 3721 (1901).
[6] St. v. Kostanecki, Tambor and Rozycki: Ibid., 34, 3721 (1901).
[7] With other colorless aromatic compounds, pyrocatechuic acid, for instance, I was able to show the formation of colored lakes.

exerts only a slight influence upon the properties of a compound save when it is accompanied by a perceptible displacement of the atoms in space and a consequent change in the tension of the molecule. A typical instance of this is to be found in the flavanoles[1] whose marked fluorescence is less affected by substitution than is the case with the xanthones and the flavones. The explanation is that they act like a ring system in which two benzenes are connected by means of an interwoven γ-pyrone furan ring (cf. p. 390).

How do the other fluorescing substances act? A glance over the examples in Table II shows that the fluorescing compounds with salt-forming groups generally contain two such groups, usually arranged symmetrically, one of which is as far as possible from the chromophore. Thus in the fluorescing acridines, pyronines, thiopyronines, thiodiphenylamines, phenazines, phenoxazines, fluoresceines (in alkaline solution), etc., one amino or hydroxyl group is in the para position to the nitrogen or carbon atom having the double bond, while the other salt-forming group acts also as a chromophore, at any rate with quinoid dye-stuffs and their salts. This latter salt-forming group does not count at all as producing fluorescence but only as a chromophore. In fact it works against the fluorescence even when it is the otherwise favorable amino group, because the effect of a chromophore is greater than that of a salt-forming group. For this reason, in most fluorescing dyes, only one of the salt-forming groups is of importance to the fluorescence. It is always the one which has no double bond and which is in the para position to a carbon or nitrogen atom having a double bond. If this salt-forming group is absent, the compound ether has no fluorescence or much less than the substance from which it is derived. Instances of this are phosphine (chrysaniline), aposafranine, the indulines, New-Blue and others. If it is the other salt-forming group which is absent, as in rosinduline, the fluorescence remains. The strong fluorescence of the unsymmetrical rosinduline is an argument against

[1] St. v. Kostanecki, Lampe, Tabor and co-workers.

symmetry relations being of importance to fluorescence. Fluorescence is not due in some mysterious way to the presence of two salt-forming groups in the "fluoresceine position" because a single salt-forming group may be entirely equivalent to the two, provided it is in the para position with reference to the chromophore and has no double bond. The enormous increase in fluorescence, which R. Meyer has shown for xanthone when the two symmetrical positions 3 and 6 are occupied, is in favor of the view that the 3-6-dioxyxanthone, in contradistinction to the other oxyxanthones, reacts in the enol form as oxyformofluoresceine and not in the keto form as a xanthone. The intense fluorescence of tetramethyldiáminoxanthone is to be explained in the same way. The ready oxidizability of the pyronines to this compound seems to me an argument in favor of the enol formula.

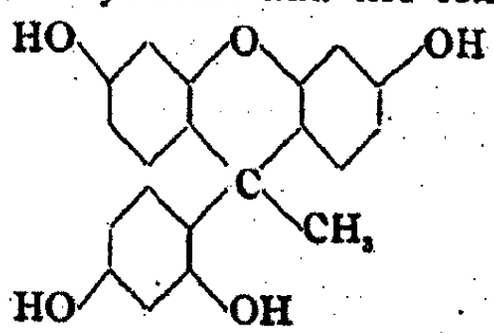
Of the regularities discussed in detail for the xanthones and flavones, one seems to hold for all fluorescing substances, namely that *fluorescence is most marked when a salt-forming group is in the farthest position from the chromophore.* Whether the other rules are of general application unfortunately cannot be told until the other classes of fluorescing substances have been studied as systematically as the xanthones and flavones. Even the fluoranes are not well enough known to be used with safety. It is true that R. Meyer has shown for this group[1] that a maximum fluorescence is obtained when the salt-forming groups are in the "fluoresceine position" (with a hydroxyl therefore in the para position to the double bond) while the fluorescence is destroyed when they are in the hydroquinone phthaleine position. Meyer has also brought together instances from the literature wherein homologous resorcinols show the fluoresceine reaction and are therefore to be looked upon as fluoresceines. As to this last point one is certainly justified in assuming the formation of genuine fluorane derivatives for cresorcinol and orcinol and this is probably true for

[1] R. Meyer: Zeit. phys. Chem., 24, 468 (1897).

dioxy-*o*-xylene. On the other hand, there is strong reason to doubt the fluoresceine nature of the condensation products of 1.2.6-dioxytoluene, 1.3.2.4- and 1.3.4.6-dioxy-*m*-xylene, and mesorcinol. As we are dealing with substances which have never been isolated, only the two following reasons can be urged for their general fluoresceine nature: First, the substances in question are formed in presence of phthalic anhydride and second, they show the fluoresceine reaction. The first reason is not conclusive so long as it is not proved that phthalic anhydride actually enters into the molecule of the new compound and that it is not a question of the condensation products of the resorcinol component. The proof for the participation of phthalic anhydride in the reaction has not been furnished; on the contrary it has been proved for resorcinol that the condensation product is formed in presence of sulphuric acid without any phthalic anhydride being there. From this follows that the condensation product of resorcinol, and probably the analogous one of xylorcinol, has not a structure like fluoresceine. One should also not lay too much importance on the second test, the fluoresceine reaction, because substances which have nothing to do with fluoresceine show a very similar fluorescence. How careful one must be in such conclusions from analogy was brought home to me by experiments which I will describe here because the compounds I obtained possibly stand in close relation to the condensation products cited by R. Meyer.

During the preparation of resacetophenone there is obtained as by-product a red tar which contains a fluorescing unidentified dye-stuff in addition to the non-fluorescing resaceteine, first described by Nencki and Sieber, and made synthetically a few years ago by Bülow. The resemblance between the fluorescence of this unknown substance and that of fluoresceine made me think that possibly the compound had a structure similar to that of fluoresceine. This might have been the case if the carbonyl of the resacetophenone had taken over the properties of the carbonyl of phthalic anhydride

and had reacted with two molecules of resorcinol. My guess that the fluoresceine dye-stuff had the following constitution



seemed to be confirmed when I obtained a fluoresceine-like fluorescing condensation product by fusing resorcinol and resacetophenone with $ZnCl_2$. As a check, however, I fused resorcinol alone with zinc chloride and obtained a red tar with exactly the same fluorescence. It is thus proved that resacetophenone does not take part in the reaction. It is quite possible that the condensation product is identical with the fluorescing dye-stuff obtained during the preparation of resacetophenone and it is also possible that it is a lower homologue of one or more of the condensation products obtained by R. Meyer. Guesses as to the constitution of these substances are of course useless so long as these compounds have not been prepared pure and analyzed.

As a system can take up from the surrounding medium chiefly those vibrations corresponding in period with those which it possesses itself, the observation of the absorption of rays of definite wave-length or definite oscillation frequencies may give a clue as to the rate of oscillation of the smallest particles. All true benzene derivatives have absorption bands in the ultra-violet.[1] Consequently by a suitable substitution of atoms and groups one might expect to change the frequency of the vibrating particles of any benzene derivatives so much that these vibrating particles should cause either pulsations in the ultra-violet close to the edge of the visible spectrum or should absorb those of the visible spectrum. One would obtain fluorescing substances, or by adding chromophoric

[1] The breaking of one double bond is enough to destroy the ultra-violet absorption.

groups, colored substances simply by a suitable tying of benzene radicals either together or to other groups of atoms. The formation of "groups fluorophoric by themselves," as understood by R. Meyer, appears to me of no importance for producing fluorescence.

According to R. Meyer, the γ-pyrone ring[1] is the cause of the fluorescence in the xanthones and flavones, and Meyer bases this assumption on the fact that the appearance of fluorescence goes hand in hand with the closing of the γ-pyrone ring. It appears to me, however, that the assumption of a special fluorescent group is not the only way to account for the appearance of fluorescence when the γ-pyrone ring closes. One can ascribe the fluorescence of the xanthones and the fluoranes to the fact that the two benzene nuclei are connected in the ortho position. This special structure might cause the fluorescence, and the formation of the γ-pyrone ring would then be looked upon as a purely accidental coincidence.

The following compounds also show fluorescence.[2]

TABLE II

Name	Salt group	Fluorescence
Fluorene		violet
Fluorenalcohol		
Phenylfluorene		
Carbazolic acid		
Thiodiphenylamine		
Methylene blue	$N(CH_3)_2$	very faint
Lauth's violet	NH_2	very strong
Thionoline	NH_2	" "
Thionol	OH	" "
Acridone		intense blue
Dinaphthacridine		
Acridine		

[1] R. Meyer: Zeit. phys. Chem., 24, 477, 491 (1897).

[2] The instances cited in Table II are taken from Krafft's Lehrbuch der organischen Chemie, Beilstein's Handbuch, R. Meyer's paper [Zeit. phys. Chem., 24, 468 (1897)] and some original sources in Berne dissertation sand the Berichte. After the names of some of the compounds are given the salt-forming group on which the fluorescence depends.

TABLE II—(*Continued*)

Name	Salt group	Fluorescence
Methylacridine		
Acridic acid		
Acridic aldehyde		
Acridine yellow	NH_2	
Acridine orange	$N(CH_3)_2$	
Phenylacridine		
Benzoflavine	NH_2	very strong
Acridine orange R	$N(CH_3)_2$	" "
Phosphine		very faint
Pyronine	$N(CH_3)_2$	as in the rhodamines
Formofluoresceine	OH	as in the fluoresceines
Leuco base of rosamine		
Fluorane		very strong
Fluoresceine (in alkaline solution)	OH	very strong
Eosine (in alkaline solution)	OH	" "
Rhodamines and anisolines	NR_2	" "
Thiopyronine	NR_2	
Phenacines	NR_2	
Phenosafranine	NH_2	yellowish red
Rosinduline [1]	NH_2	
Rosinduline [2]	NH_2	fiery
Toluylene red	$N(CH_3)_2$	
Magdala red	NH_2	
Phenofluorindine		yellow in alcohol or benzene
Diphenylfluorindine		
Phenoxazine		
Resorufine	OH	fiery
Iris-blue	OH	"
Base of Nile-blue		in ether and alcohol
Base of new blue		only in alcohol
Naphthanthracene		greenish yellow
Dihydroanthracene		dark blue in benzene and toluene
Dichloranthracene		
Anthracene		blue
Anthranol		bluish
Oxyanthranol		yellowish green
Hydroquinizarine		
Methylphenylanthracene		
Phenolphthalidine		
Anthraquinoline		deep blue
Phenanthrene		

TABLE II—(*Continued*)

Name	Salt group	Fluorescence
Phenanthridine		
Chrysene		deep reddish violet
Picene		
Mono-, di- and tri-chlor-pyrene		
Dithioxanthion		yellow in H_2SO_4
Dithiofluorane		faint greenish
Thiofluoresceine	OH	" "
Xanthion		deep green in H_2SO_4
Xanthene		green
Xanthhydrol		"
Xanthone		
2.7-dimethylxanthone		beautiful bluish green
3.6-dimethylxanthone		" " "
4.5-dimethylxanthone		" " "
Dixanthylene		dark blue in benzene and toluene
Tetramethyl dixanthylene		dark blue in benzene and toluene
α-phenonaphthoxanthone		beautiful greenish blue in H_2SO_4
Oxyphenonaphtho-xanthone [1]		
Oxyphenonaphtho-xanthone [2]		faint greenish in H_2SO_4
Tolunaphthoxanthone [1]		green to bluish green in H_2SO_4
" [2]		green to bluish green in H_2SO_4
" [3]		green to bluish green in H_2SO_4
" [4]		
Methyldinaphthoxanthene		greenish to bluish-green in H_2SO_4
Dinaphthoxanthene		beautiful light green
o-dixanthone		greenish in H_2SO_4
Dixanthone		" " "

In all the cases cited in Table II R. Meyer claims that the fluorescence depends on the presence of 'fluorophoric groups.' He assumes therefore that the formation of the most hetero-cyclic ring (pyrone-, azine-, oxazine-, thiazine-ring, etc.) causes

the fluorescence.[1] A heterocyclic ring as such is not a sufficient explanation of fluorescence because in heterocyclic rings there is no ultra-violet absorption, the fundamental condition for fluorescence. R. Meyer says himself that 'fluorophoric groups' become effective only when between benzene nuclei.[2] Thus he could only show fluorescence with the γ-pyrone ring when this was united with two phenyl radicals.[3]

R. Meyer therefore assumes that the power of fluorescing is latent in the heterocyclic ring and that it becomes effective only when the ring is connected with two phenyl radicals. Now latent fluorescence can only mean a fluorescence in which both the absorbed and the emitted rays lie in the ultra-violet. In any case a latent power of fluorescence cannot be separated from the conception of absorption and as it is inconsistent with the actual absorption of the heterocyclic rings, it follows that the γ-pyrone ring, the azine ring, oxazine ring, the thiazine ring, etc., cannot be considered as the cause either of a visible or of a latent fluorescence. Quite apart from theoretical considerations, the observations of γ-pyrone and diphenyl-γ-pyrone can be interpreted in a different way from that adopted by R. Meyer.

From these observations one may deduce, first, that the γ-pyrone ring has no effect on fluorescence and, second, that fluorescence is caused by the two phenyl radicals. If one is to speak at all of 'fluorophoric' groups, the benzene radicals have the best title to such a name. The phenyl rings are conspicuous for their marked absorption of ultra-violet rays; they possess to a high degree what R. Meyer calls 'latent power of fluorescence'; and consequently they are the true causes of the fluorescence.

Since a phenyl radical by itself vibrates very rapidly and therefore absorbs rays in the extreme ultra-violet, the fluo-

[1] Zeit. phys. Chem., 24, 508 (1897).
[2] Ibid., 24, 508 (1897).
[3] Ibid., 24, 477 (1897).

rescence is entirely in the ultra-violet. The fluorescence can, however, be brought into the visible portions of the spectrum by increasing the period of vibration of the particles. This can be accomplished in several ways:

First, by the use of solvents having very high dispersive powers. Since such solvents obviously represent dense media, it seems plausible that vibrating particles should be checked by the resistance of the medium and should oscillate less rapidly. In consequence they absorb rays of greater wavelength and the fluorescence may therefore fall within the visible spectrum.

Second, by introduction of chromophores and bathochrome salt-forming groups. Since the groups displace the absorption bands towards the red end of the spectrum they may aid in making visible a fluorescence lying far out in the ultra-violet spectrum although, for the same reason, they tend to destroy a previously visible fluorescence[1]. For substances which have latent fluorescence, we have a reversal of the generalizations previously pointed out in regard to chromophores and salt-forming groups. In reality the reversal is only apparent.

The narrow limits of sensibility of the eye are alone responsible for the same process, the displacement of the absorption bands towards the red end of the spectrum decreasing the visibility of fluorescence for substances which have a visible fluorescence and increasing the visibility of the fluorescence for substances which have an invisible, latent or ultra-violet, fluorescence.

Third, by uniting benzene radicals in definite ways. This third point appears to be of more importance than the other two, for a large number of substances fluoresce without chromophoric groups and in solvents of low dispersion, while it is by no means certain that a solvent alone or the presence of chromophores alone is sufficient to displace the absorption bands of the phenyl nuclei into the visible spectrum. It

[1] Through the bathochrome displacement, the fluorescence may be carried partially or entirely into the ultra-red.

seems to me that the additional action of one of the types of grouping to be mentioned can never be excluded entirely.

The most general way in which the phenyl radicals are joined in fluorescing substances is that of the ortho position, connection being made by one or more intermediate groups. All the fluorescent substances in Table II belong to this type. Frequently one also finds in fluorescing substances that the adjacent carbon atoms of one phenyl nucleus are connected by other groups to a carbon atom which is joined directly to a second phenyl radical. The substances in Table III belong under this heading.

TABLE III

Name	Fluorescence	Name
Flavone.....	violet-blue in H_2SO_4	Diphenyl indol
Naphthoflavone.....	green in H_2SO_4	Oxytoluoxazol
Naphthoflavanone	blue in alcohol	γ-Phenyl quinoline and α- and β-amido derivatives
3′-4′-methylenedioxy-naphthoflavone.....	" " "	α-Phenyl quinic acid
2-ethoxyflavanone	" " "	Azonium base of quinoxaline[3]
3-ethoxy-4′-methoxy-flavanone[1]	" " "	
Dihydroquinoxaline[2]...	yellowish	

Diphenyl-γ-pyrone belongs to a third type, which does not have so many representatives as the preceding two. Here the carbon atoms carrying the two phenyl radicals are connected by two chains. In this class is to be placed α-diphenyl pyrrol.

These three types of fluorescing substances are connected and the last two can be deduced from the first, if the function of the two adjacent atoms in the benzene radical be considered as transferred to the carbon atom carrying the phenyl nucleus. If two adjacent carbon atoms of the same benzene

[1] This and the preceding compounds prepared by v. Kostanecki and his pupils.

[2] l. c., page 373.

ring are considered as replaced by one carbon atom carrying a benzene radical, we pass from the first type to the second, from xanthone for instance to flavone. If two pairs of adjacent carbon atoms of the phenyl group are each replaced by a carbon atom carrying a benzene ring we come to the third type, represented by the diphenyl-γ-pyrone. Flavone therefore is intermediate in type with xanthone and diphenyl-γ-pyrone.

The first two types include the large majority of fluorescing substances and are derived from the same fundamental type in which two ortho carbon atoms of a phenyl nucleus are joined together by means of other groups. Quite a number of fluorescing substances belong to this basal type[1], Table IV.

TABLE IV

Name	Fluorescence	Name
β-Naphthindol[2]	green-blue	α-Naphthylamine
2-3-Dimethylnaphthindol[2]	violet in alcohol	α-Phenylnaphthylamine
Indoxyl	yellow-green in water	α-Dimethylnaphthylamine
β-Methyl chromone[3]	faintly blue-violet	β-Naphthylamine
β-Methyl-3-oxychromone	strongly blue-violet	β-Phenylnaphthylamine
β-Methyl-2-oxychromone	beautiful blue	β-Dimethylnaphthylamine
Esculine	blue	β,β-Dinaphthylamine
Quinine	blue	Methyl benzoxazol methyl-ketol

TABLE V

Name	Fluorescence
Orthocumaric acid	green
Orthoamidocinnamic acid	blue-green
Ethyl *o*-amidocinnamate	yellow-green
Hydroquinone dicarboxylic acid and its dimethyl ester.	blue
Anthranilic acid	violet

[1] This type differs from the two derived from it, by having fewer phenyl groups. Curiously enough it is the substances belonging in this class for which we have the reversal of the generalizations in regard to the effect of chromophores and salt-forming groups. Excellent instances of this are to be found in the chromones prepared synthetically by v. Kostanecki and his pupils, and also in esculine which has two adjacent hydroxyls. This reversal of the generalizations is even more marked in the compounds with open side chains.

[2] These two compounds and the naphthalene compounds in the third column have a double bond in the ortho position.

[3] Prepared by v. Kostanecki and his pupils.

From these compounds we pass to a class apparently differing radically from those previously under consideration to a group with open side chains. In this class we find the bluish green fluorescence of *o*-amidocinnamic acid, a compound differing from those of the indol group by the broken ring. For the free acid one could of course assume an intramolecular re-arrangement forming an ammonium salt and closing the ring. This, however, would not do as an explanation for the fluorescence of the derivatives of the *o*-amidocinnamic acid, for instance the ethyl ester with its yellowish green fluorescence. The *o*-amidosuccinic acid is by no means the only case in which fluorescence occurs with an open side chain.

Though this phenomenon appears surprising at first sight there are two things to be kept in mind. The first is that, as I have already pointed out[1] and have proved by other observations, the closing of a ring sometimes has but little effect on the properties of a substance[2]. An open ring can behave like a closed one if, according to Baeyer's tension theory, the end members come so close together that the closing of the ring has practically no effect on the position of the carbon atoms. For this to occur it is necessary, however, that the side chains are in the ortho position relatively to each other. In this case there is the possibility of the properties and also the fluorescence of a closed ring system reniaining much the same even after the ring breaks.

The second point to keep in mind is that the fluorescing substances with open side chains have a high dispersion. This is especially true for the *o*-oxy- and *o*-amidocinnamic acids and their derivatives. According to Brühl the cinnamyl compounds have enormously high dispersion constants, because they have the carbonyl and ethylene groups adjoining (as complex chromophore O : C . C : C) and connected directly to a phenyl radical.

The violet and the blue fluorescence of *p*-*p*-dimethoxystilbene and α-diphenylbutadien respectively may be referred

[1] p. 379.

[2] This comes out clearly if we compare Δ-tetrahydrophthalic acid with xeronic acid. The two compounds are similar in every respect (Krafft, p. 397).

to the occurrence of a double bond in direct connection with two phenyl nuclei. There is also the possibility that these compounds behave like systems with closed rings in which case they would come under the first and second types.

The main points of this paper may be summed up as follows:

I. The fluorescence of a substance can be decreased or destroyed by a complementary coloring. It is immaterial whether the coloring is due to the compound itself or to impurities.

II. The visible fluorescence is usually decreased by the introduction of chromophoric groups: (*a*) because the chromophore determines the color and may decrease the fluorescence by producing a complementary color; (*b*) because the chromophore displaces the absorption bands towards the red end of the spectrum, thus decreasing the possibility of fluorescence.

III. Salt-forming groups affect fluorescence, usually unfavorably. (1) They displace the absorption bands towards the red end of the spectrum except in a few cases, such as the hypsochrome amino group for instance, which, as a matter of fact, increases the fluorescence. (2) They often re-enforce the coloring effects of the chromophores. (3) They increase the effect of the chromophores in displacing the absorption bands towards the red end of the spectrum. This increased effect is more marked the nearer the chromophore and the salt-forming groups. The same is true for the mutual effect of two salt-forming compounds.

In accord with this is the behavior of the oxyxanthones and oxyflavones, where every one of the fluorescent substances which has a salt-forming group at all, has it in the remotest possible position from the chromophore.

IV. The latent fluorescence, characteristic of all benzene derivatives, can be made visible by the same means which decrease the visible fluorescence, namely, by the introduction of chromophores and salt-forming groups.

V. More effective than chromophores or bathochrome salt-forming groups is the uniting of two phenyl nuclei in the ortho position or in a way analogous to this.

Berne, 1906.

ON THE GENERAL EQUATIONS OF THE THEORY OF SOLUTIONS

BY J. E. TREVOR.

The formation of a solution from its components. The dilution of a solution. The condition of equilibrium for coexistent solution and vapor when one of the components is involatile. Osmotic pressure. The reversible dilution of a solution.

The formation of a solution from its components

The operator Δ

It is intended in the following pages to present the general thermodynamic theory of solutions, in particular the theory of solutions, one of whose components is relatively involatile, in a way that it is hoped will more clearly than is usual bring out the meaning of the relations that are obtained.

Let M_1, M_2 be the masses of the two independent components C_1, C_2 of a liquid mixture, a solution, in stable thermodynamic equilibrium under the pressure p at the absolute temperature θ. Let the functions E, F, G, H, V, S of the variables

$$p, \qquad \theta, \qquad M_1, \qquad M_2$$

be the energy, the free energy, the heat function, the thermodynamic potential, the volume, and the entropy of the solution. Let the symbols

$$\Delta E, \qquad \Delta F, \qquad \Delta G, \qquad \Delta H, \qquad \Delta V, \qquad \Delta S$$

denote the changes of the energy, etc., of the system composed of the masses M_1, M_2 when these masses, taken in stable equilibrium at p, θ, are irreversibly or reversibly mixed to form the stable solution at p, θ. The changes in question are thus defined by the equations

$$(1) \qquad \begin{cases} \Delta E = E - M_1 e_1 - M_2 e_2 \\ \cdot \quad \cdot \quad \cdot \\ \Delta S = S - M_1 s_1 - M_2 s_2, \end{cases}$$

where e_j, f_j, g_j, h_j, v_j, s_j, denote the specific energy, etc., of the component C_j. The quantities E . . S being homogeneous and of the first degree in M_1, M_2, and the small letters being functions of p, θ, it is seen that the quantities ΔE . . ΔS are to be regarded as functions of

$$p, \qquad \theta, \qquad M_1, \qquad M_2,$$

and that they are homogeneous and of the first degree in M_1, M_2.

The three relations between the quantities just defined

If we replace the quantities

$$F, \qquad G, \qquad H, \qquad f_j, \qquad g_j, \qquad h_j,$$

in the last three of the equations (1), by their values as expressed by the equations defining these quantities,

$$\begin{aligned} F &= E - \theta S & f_j &= e_j - \theta s_j \\ G &= E + pV & g_j &= e_j + pv_j \\ H &= E + pV - \theta S & h_j &= e_j + pv_j - \theta s_j, \end{aligned}$$

we find, after rearranging the terms, the three independent equations

$$(2) \qquad \begin{cases} \Delta F = \Delta E - \theta.\Delta S \\ \Delta G = \Delta E + p.\Delta V \\ \Delta H = \Delta E + p.\Delta V - \theta.\Delta S. \end{cases}$$

Interpretation of the terms

The first two of the above equations may be written

$$(3) \qquad \begin{cases} \Delta E = \Delta F + \theta.\Delta S \\ \Delta E = -p.\Delta V + \Delta G. \end{cases}$$

It is obvious that ΔE is the change of the energy of the system composed of the masses M_1 and M_2 when the mixture is formed from its components at p, θ; that $\theta.\Delta S$ is the heat absorbed by the system when the process is reversibly conducted; and that $-p.\Delta V$ is the work absorbed when the process is wholly irreversible. By the first law of thermodynamics, it follows that ΔF is the reversible work of the change of state, and that ΔG is the irreversible heat. It may further be noted

that the "dissipation," the energy dissipated (instead of being developed as work) in the irreversible process, which is

$$-(\Delta F) - (p.\Delta V) = -(\Delta F + p.\Delta V) = -\Delta H,$$

is the quantity $-\Delta H$.

Assembling these interpretations, it appears that, in the change considered,

ΔE = change of energy	ΔF = reversible work
$-p.\Delta V$ = irreversible work	$\theta.\Delta S$ = reversible heat
ΔG = irreversible heat	$-\Delta H$ = dissipation

From the three independent relations

$$(4a)\qquad \begin{cases} \Delta E = +\Delta F + \theta.\Delta S \\ \Delta E = -p.\Delta V + \Delta G \\ \Delta E = -p.\Delta V + \Delta H + \theta.\Delta S \end{cases}$$

between the reversible and irreversible work and heat, the energy change, and the dissipation, of the formation of the solution from its components at p, θ, four further relations may be deduced, by eliminating common terms between the three equations and between pairs of the equations. We thus obtain,

$$(4b)\qquad \begin{cases} \Delta E = \Delta F - \Delta H + \Delta G \\ o = \Delta F + p.\Delta V + \theta.\Delta S - \Delta G \\ o = \Delta F - \Delta H + p.\Delta V \\ o = \Delta H + \theta.\Delta S - \Delta G. \end{cases}$$

The main facts expressed by these equations are that the energy-development in the formation of the solution from its components is equal to the dissipation together with the development of irreversible work and of reversible heat, that (still speaking of energy *development*) the irreversible work and the dissipation together equal the reversible work, and that the reversible heat and the dissipation together equal the irreversible heat.

The derivatives of the dissipation

By differentiating the equation defining the (negative) dissipation,

$$\Delta H = H - M_1 h_1 - M_2 h_2,$$

and comparing with the general equations

$$dH = Vdp - Sd\theta + \mu_1 dM_1 + \mu_2 dM_2$$
$$dh_j = v_j dp - s_j d\theta,$$

where μ_j is the potential of C_j, we find

$$(5) \qquad \frac{\partial \Delta H}{\partial p} = \Delta V, \qquad \frac{\partial \Delta H}{\partial \theta} = -\Delta S, \qquad \frac{\partial \Delta H}{\partial M_j} = \mu_j - h_j.$$

The relation of the dissipation to the reversible work and to the irreversible heat

The equations connecting the dissipation with the reversible work and the irreversible heat,

$$\Delta H - p.\Delta V = \Delta F$$
$$\Delta H + \theta.\Delta S = \Delta G,$$

may now be written

$$\Delta H - p\frac{\partial \Delta H}{\partial p} = \Delta F$$

$$\Delta H - \theta\frac{\partial \Delta H}{\partial \theta} = \Delta G,$$

or, in better form,

$$(6) \qquad \begin{cases} \dfrac{\partial}{\partial p}\dfrac{\Delta H}{p} = -\dfrac{\Delta F}{p^2} \\ \dfrac{\partial}{\partial \theta}\dfrac{\Delta H}{\theta} = -\dfrac{\Delta G}{\theta^2}. \end{cases}$$

These equations express the relations of the dissipation to the reversible work and to the irreversible heat.

The dilution of a solution

The work and heat of a dilution

Consider the irreversible or reversible dilution of the solution whose mass is $M_1 + M_2$, by the addition of the mass dM_j of C_j to the solution at p, θ. If we write Ψ for the energy, or free energy, etc. of the solution, and write ψ_j for the corresponding specific extensive quantity for the j-th component,

the value of the extensive quantity for the system composed of the masses $M_1 + M_2$ and dM_j will be

$$\Psi + \psi_j dM_j$$

before the operation, and

$$\Psi + \frac{\partial \Psi}{\partial M_j} dM_j$$

after the operation. In the operation, therefore, the rate of change of the quantity, per unit increase of the mass of C_j in the solution, is

$$\frac{\partial \Psi}{\partial M_j} - \psi_j,$$

which is the function

$$\frac{\partial \Delta \Psi}{\partial M_j}.$$

We thus observe that, in the operation of dilution,

$$\frac{\partial \Delta E}{\partial M_2} = \text{Rate of change of the energy}$$

$$-p\frac{\partial \Delta V}{\partial M_2} = \text{“ “ addition of irreversible work}$$

$$\frac{\partial \Delta G}{\partial M_2} = \text{“ “ addition of irreversible heat}$$

$$\frac{\partial \Delta F}{\partial M_2} = \text{“ “ addition of reversible work}$$

$$\theta\frac{\partial \Delta S}{\partial M_2} = \text{“ “ addition of reversible heat}$$

$$-\frac{\partial \Delta H}{\partial M_2} = \text{“ “ dissipation.}$$

These rates may be regarded as the quantities appertaining to the addition of unit mass of C_j to a relatively great mass of the solution. The function $\partial \Delta G/\partial M_j$, the “heat of dilution” of the solution by the j-th component, shall hereafter be denoted by Δ_j. The relations that obtain between these rates may be obtained by differentiating the equations (4) and (6) with regard to M_j.

The heats of dilution

From the circumstance that the function ΔG is homogeneous and of the first degree in M_1, M_2, we find, by Euler's theorem of homogeneous functions, that

$$\Delta G = M_1\Delta_1 + M_2\Delta_2, \tag{7}$$

i. e. that the heat of mixing is a linear function of the heats of dilution.

Further, the functions Δ_j are homogeneous and of the zero degree in M_1, M_2, wherefore

$$M_1 \frac{\partial \Delta_j}{\partial M_1} + M_2 \frac{\partial \Delta_j}{\partial M_2} = 0. \tag{8}$$

By differentiation of (7) we find the further relations

$$M_1 \frac{\partial \Delta_1}{\partial M_j} + M_2 \frac{\partial \Delta_2}{\partial M_j} = 0; \tag{9}$$

and by elimination between (8), (9), we find

$$\begin{cases} \dfrac{\partial \Delta_1}{\partial M_2} = \dfrac{\partial \Delta_2}{\partial M_1} \\ \dfrac{M_1}{M_2}\dfrac{\partial \Delta_1}{\partial M_1} = \dfrac{M_2}{M_1}\dfrac{\partial \Delta_2}{\partial M_2}. \end{cases} \tag{10}$$

If the Δ_j be regarded as functions of p, θ, m_1, where m_1 is the mass of C_1 in unit mass of the solution, the equations (9) and (10) reduce to

$$m_1 \frac{\partial \Delta_1}{\partial m_1} + (1 - m_1)\frac{\partial \Delta_2}{\partial m_1} = 0. \tag{11}$$

The condition of equilibrium for coexistent solution and vapor when one component is involatile

The condition of equilibrium

The condition of equilibrium for coexistent solution and vapor, when the component C_1 is relatively involatile, may be made to yield for the "dissipation of dilution"

$$-(\mu_2 - h_2)$$

(of dilution by the volatile component C_2) an expression susceptible of experimental determination. If we write $p_o)\theta)$

for the vapor-pressure of the pure volatile component, $p_1(\theta,m_1)$ for the vapor-pressure of the solution, and distinguish extensive quantities relating to the vapor by a subscript a, the conditions of equilibrium between C_2 and vapor and between solution and vapor are

$$(12) \qquad \begin{cases} h_2(p_0, \theta) = h_a\,(p_0, \theta) \\ \mu_2(p_1, \theta, m_1) = h_a\,(p_1, \theta). \end{cases}$$

In order to reach an expression for $\mu_2 - h_2$, we note that

$$h_2 - h_2\,(p_0, \theta) = \int_{p_0} v_2\,(p, \theta)\,dp$$

$$\mu_2 - \mu_2\,(p_1, \theta, m_1) = \int_{p_1} \phi_2\,(p, \theta, m_1)\,dp.$$

Here we write

$$\phi_2 = \partial V/\partial M_2,$$

which is equal to $\partial\mu_2/\partial p$. In each equation the upper limit of the integral is the general value p of the pressure. Eliminating the first members of (12) by means of these equations, we get

$$h_2 - \int_{p_0} v_2\,dp = h_a\,(p_0, \theta)$$

$$\mu_2 - \int_{p_1} \phi_2\,dp = h_a\,(p_1, \theta);$$

whence, by subtraction,

$$-(\mu_2 - h_2) = \int_{p_0} v_2\,dp - \int_{p_1} \phi_2\,dp + \int_{p_1}^{p_0} v_a\,dp$$

$$= \int_{p_0} v_2\,dp - \int_{p_1}^{p_0} \phi_2\,dp - \int_{p_0} \phi_2\,dp + \int_{p_1}^{p_0} v_a\,dp$$

$$= \int_{p_1}^{p_0} (v_a - \phi_a)\, dp + \int_{p^0}^{} (v_2 - \phi_2)\, dp.$$

Writing J for the second member of the last equation, we obtain, as desired,

$$(13) \qquad -(\mu_2 - h_2) = \mathrm{J}.$$

It thus appears that, when the solution is under the pressure p_0, the dissipation of dilution by the volatile component reduces to

$$\int_{p_1}^{p_0} (v_a - \phi_2)\, dp.$$

The relation of the reversible work and the irreversible heat to the dissipation

Making use of equations (5) and (13), we have

$$d\Delta\mathrm{H} = \Delta\mathrm{V}.dp - \Delta\mathrm{S}.d\theta + (\mu_1 - h_1)\, d\mathrm{M}_1 - \mathrm{J}d\mathrm{M}_2;$$

whence follow

$$(14) \qquad \frac{\partial \Delta\mathrm{V}}{\partial \mathrm{M}_2} = -\frac{\partial \mathrm{J}}{\partial p}, \qquad \frac{\partial \Delta\mathrm{S}}{\partial \mathrm{M}_2} = +\frac{\partial \mathrm{J}}{\partial \theta}.$$

Now, with reference to dilution by the volatile component C_2, the general equations (for work and heat *development*).

Rev. work = Irr. work + Dissipation
Irr. heat = Rev. heat + Dissipation

are the equations

$$\frac{\partial \Delta\mathrm{F}}{\partial \mathrm{M}_2} = -p\frac{\partial \Delta\mathrm{V}}{\partial \mathrm{M}_2} - \mathrm{J}$$

$$\Delta_2 = +\theta\frac{\partial \Delta\mathrm{S}}{\partial \mathrm{M}_2} - \mathrm{J},$$

which are converted by (14) to

$$(15) \qquad \begin{cases} \dfrac{\partial}{\partial p}\dfrac{\mathrm{J}}{p} = \dfrac{1}{p^2}\dfrac{\partial \Delta\mathrm{F}}{\partial \mathrm{M}_2} \\ \dfrac{\partial}{\partial \theta}\dfrac{\mathrm{J}}{\theta} = \dfrac{\Delta_2}{\theta^2}. \end{cases}$$

Assembling the formulations by means of the expression J, we have, for the dilution:

$$\text{Dissipation:} \quad -\frac{\partial \Delta H}{\partial M_2} = J$$

$$\text{Irr. work:} \quad -p\frac{\partial \Delta V}{\partial M_2} = p\frac{\partial J}{\partial p}$$

$$\text{Rev. heat:} \quad \theta\frac{\partial \Delta S}{\partial M_2} = \theta\frac{\partial J}{\partial \theta}$$

$$\text{Rev. work:} \quad \frac{\partial \Delta F}{\partial M_2} = p^2\frac{\partial}{\partial p}\frac{J}{p}$$

$$\text{Irr. heat:} \quad \frac{\partial \Delta G}{\partial M_2} = \theta^2\frac{\partial}{\partial \theta}\frac{J}{\theta}.$$

The last of these equations, namely

$$(16) \qquad \frac{\Delta_2}{\theta^2} = \frac{\partial}{\partial \theta}\left(\frac{1}{\theta}\int_{p_1}^{p}(v_a - \phi_2)\,dp + \frac{1}{\theta}\int_{p_0}^{}(v_2 - \phi_2)\,dp\right),$$

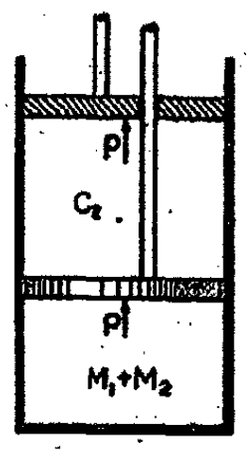
is the *general* form of the equation for the heat of the dilution

$$\Delta_2\,(p, \theta, m_1).$$

Osmotic pressure

The condition of osmotic equilibrium

Suppose a solution whose component-masses are M_1, M_2 to be separated from a mass of the liquid component C_2 by a piston permeable only by C_2; and suppose this system of masses, under the pressure p and at the temperature θ, to be maintained in equilibrium by a force applied to the semipermeable piston to balance the osmotic pressure P. Let an infinitesimal decrease of this force effect an addition of the mass dM_2 to the solution at constant p, θ, M_1.



Before this addition the energy of the system composed of the masses

$$M_1 + M_2 \quad \text{and} \quad dM_2$$

is

$$E + e_2 dM_2.$$

After the addition the energy is

$$E + \left\{ e_2 - P \frac{\partial V}{\partial M_2} - p \left(\frac{\partial V}{\partial M_2} - v_2 \right) + \theta \left(\frac{\partial S}{\partial M_2} - s_2 \right) \right\} dM_2.$$

The rate of increase of the energy of the *solution* is, therefore,

$$\frac{\partial E}{\partial M_2} = e_2 - P \frac{\partial V}{\partial M_2} - p \left(\frac{\partial V}{\partial M_2} - v_2 \right) + \theta \left(\frac{\partial S}{\partial M_2} - s_2 \right).$$

Here

$$\frac{\partial E}{\partial M_2} = - p \frac{\partial V}{\partial M_2} + \theta \frac{\partial S}{\partial M_2} + \mu_2,$$

wherefore, by subtraction,

$$\mu_2 - (e_2 + pv_2 - \theta s_2) = - P \frac{\partial V}{\partial M_2},$$

or

$$- (\mu_1 - h_1) = P\phi_2. \tag{17}$$

This condition of the osmotic equilibrium may be regarded as the equation

$$P = P(p, \theta, m_1)$$

for the equilibrium values of the osmotic pressure.

The osmotic work is the dissipatible work

The condition of osmotic equilibrium (17) exhibits the rather obvious fact that the osmotic work of dilution,

$$P_2\phi_2,$$

is the dissipatible part

$$- \frac{\partial \Delta H}{\partial M_2} = - (\mu_2 - h_2) = P\phi_2 = J > 0$$

of the work-development of a reversible dilution. Accordingly, the relations between the osmotic work of dilution and the reversible and irreversible works and heats of the dilution are to be found by differentiating the general relations (4) with regard to M_2, and replacing the dissipation $-\partial \Delta H / \partial M_2$ by the above expression. In this way we find:

$$(18a)\qquad \begin{cases} \dfrac{\partial \Delta E}{\partial M_2} = -p\dfrac{\partial \Delta V}{\partial M_2} - P\phi_2 + \theta\dfrac{\partial \Delta S}{\partial M_2} \\ \dfrac{\partial \Delta E}{\partial M_1} = +\dfrac{\partial \Delta F}{\partial M_1} + P\phi_1 + \Delta_1 \\ o = +\dfrac{\partial \Delta F}{\partial M_2} + P\phi_2 + p\dfrac{\partial \Delta V}{\partial M_2} \\ o = -P\phi_2 + \theta\dfrac{\partial \Delta S}{\partial M_2} - \Delta_2; \end{cases}$$

and also, from equations (6),

$$(18b)\qquad \begin{cases} \dfrac{\partial}{\partial p}\dfrac{P\phi_2}{p} = \dfrac{\partial \Delta F/\partial M_2}{p^2} \\ \dfrac{\partial}{\partial \theta}\dfrac{P\phi_2}{\theta} = \dfrac{\Delta_2}{\theta^2}. \end{cases}$$

The physical interpretation of these equations is too obvious to require comment.

The last of these equations may be written

$$P\phi_2 = -\Delta_2 + \theta\frac{\partial P\phi_2}{\partial \theta}.$$

With a slightly different notation, Bancroft[1] quotes it in the form

$$PV = Q + T\frac{\partial PV}{\partial T},$$

and observes that it holds "under all circumstances." Yet one must bear in mind that the variables employed in this well-known equation are p, θ, M_1, M_2, *i. e.*, that the derivative is formed at constant p, m_1; and it must be understood that the equation differs from the corresponding free-energy equation of Gibbs and Helmholtz, with which it is sometimes confused. The last point may be illustrated by considering the formation of the solution. The free-energy equation relating to this operation is

$$\Delta F = \Delta E - \theta.\Delta S.$$

[1] Jour. Phys. Chem., 10, 319 (1906).

In p, , M_1, M_2 it may be written

$$\Delta F = \Delta E + \theta \frac{\partial \Delta H}{\partial \theta},$$

which is not the same thing as the relation here considered,

$$\Delta H = \Delta G + \theta \frac{\partial \Delta H}{\partial \theta}.$$

The latter equation furnishes an expression for the work subject to dissipation, the former an expression for the whole reversible work.

The equations of the general theory of solutions

If we restrict ourselves to the usually sufficient particular case $p = p_o$, the dissipation of dilution J assumes the particular value

$$I = \int_{p_1}^{p_o} (v_a - \phi_1)\, dp. \tag{19}$$

In the general theory of solutions having one relatively involatile component, the chief equations connecting quantities whose values can be experimentally determined are, for $p = p_o$, from the foregoing: The relation between the vapor-pressures p_1, p_o and the heat of dilution,

$$\frac{\partial}{\partial \theta} \frac{I}{\theta} = \frac{\Delta_2}{\theta^2}; \tag{20}$$

the relation between the osmotic pressure and the vapor-pressures,

$$P\phi_2 = I; \tag{21}$$

and the consequent relation between the osmotic pressure and the heat of dilution,

$$\frac{\partial}{\partial \theta} \frac{P\phi_2}{\theta} = \frac{\Delta_2}{\theta^2}. \tag{22}$$

The influence of the heat of dilution on the osmotic work can be expressed in another and very interesting way, by combining (20) and (21) to get

$$P\phi_2 = \theta \frac{\partial I}{\partial \theta} - \Delta_2. \tag{23}$$

Here it should not be overlooked that the equations (20), (22), and (23), namely the equations[1]

$$I - \theta \frac{\partial I}{\partial \theta} = -\Delta_0$$

$$P\phi_2 - \theta \frac{\partial P\phi_2}{\partial \theta} = -\Delta_2$$

$$P\phi_2 - \theta \frac{\partial I}{\partial \theta} = -\Delta_2,$$

are all forms of the general equation

$$-\frac{\partial \Delta H}{\partial M_2} - \theta \frac{\partial \Delta S}{\partial M_2} = -\Delta_2,$$

which corresponds to the relation, relative to the *formation* of the solution,

$$-\Delta H - \theta.\Delta S = -\Delta G,$$

and asserts that the dissipation and the reversible heat-development are together equal to the development of irreversible heat.

Evaluations

The use of experimental data in evaluating the terms of the above general equations is, of course, *illustrated* by the deduction of Kirchhoff's equation for the heat of dilution, and of van't Hoff's relation between the vapor-pressures and the composition of the solution.

For the heat of dilution we have the general equation (20),

$$\frac{\partial}{\partial \theta}\frac{I}{\theta} = \frac{\Delta_2}{\theta^2}.$$

When it is assumed, on the basis of experiment, that ϕ_2 is negligible in comparison with v_a, and that the saturated vapor of C_2 is an ideal gas, we find

[1] To which might be added the equation

$$I - \theta \frac{\partial P\phi_2}{\partial \theta} = -\Delta_2, \text{ or } \frac{\partial P\phi_2}{\partial \theta} = \frac{I + \Delta_2}{\theta}.$$

$$I = r_2 \theta \log \frac{p_0}{p_1},$$

where r_2 is the specific gas-constant for C_2. This reduces (20) to the usual approximation,

$$\frac{\partial}{\partial \theta} \log \frac{p_0}{p_1} = \frac{\Delta_2}{r_2 \theta^2} = \frac{w_2 \Delta_2}{r \theta^2},$$

where $w_2\Delta_2$ is the molecular heat of dilution, and r is the molecular gas-constant.

In the second illustration, for the osmotic work of dilution we have the general equation (21),

$$P\phi_2 = I.$$

Now, the mass M_1 being n mols of the component C_1, the number of mols per unit mass of C_2 is n/M_2. When it is assumed, on the basis of experiment, that the osmotic work of dilution $P\phi_2$ for each mol of C_1 is $r\theta$, we find

$$P\phi_2 = \frac{n}{M_2} r\theta.$$

This formulation and the above formulation for I reduce (21) to

$$\frac{n}{M_2} r\theta = r_2 \theta \log \frac{p_0}{p_1},$$

which is van't Hoff's approximation. Writing w_2 for the molecular weight of C_2, and N for M_2/w_2, and noting that $r = w_2 r_2$, we get the equation in its usual form

$$\log \frac{p_0}{p_1} = \frac{n}{N}.$$

Closer approximations than these are realizable when experiment yields better formulations of one or more of the quantities I, P, Δ_2.

The reversible dilution of a solution

A reversible process

It is well known that Kirchhoff, Helmholtz, van't Hoff, and others, have made important contributions to the theory of solutions of involatile solutes, through study of the reversi-

ble isothermal dilution effected by evaporation of a mass of the pure solvent, expansion of the resulting vapor until its pressure becomes equal to the vapor-pressure of the solution, and condensation of the mass in contact with the solution. In view of the notable employment that has been made of this process under extensive simplifying assumptions, it is natural to inquire what relation will result from a formulation of the energy change of the process when no simplifying assumptions are introduced. The relation that will result is the "condition of equilibrium" for coexisting solution and vapor, the condition namely that the potential of the solvent shall have the same value in each of the coexisting phases. This relation is the second of the above equations (12),

$$\mu_2(p_1, \theta, m_1) = h_a(p_1, \theta).$$

A demonstration of this proposition is here offered, as a supplement to the foregoing exposition of the general theory of solutions of involatile solutes.

As before, let us consider a solution consisting of the mass M_1 of an involatile solute and the mass M_2 of solvent. In its initial state, let the system undergoing the reversible isothermal change of state consist of the solution $M_1 + M_2$ and the separate mass dM_2 of solvent, both under the pressure p and at the absolute temperature θ. Let the system in its final state consist of the homogeneous mass $M_1 + M_2 + dM_2$, likewise at p, θ. For these states to be states of stable equilibrium, the value of p cannot be less than p_0, the vapor-pressure of the solvent at θ.

The reversible isothermal operation of passing from the initial to the final state of the system shall consist of the successive steps:

1. Decrease of the pressure of $M_1 + M_2$ from p to p_1;
2. Decrease of the pressure of dM_2 from p to p_0;
3. Evaporation of dM_2, at p_0;
4. Expansion of dM_2 from p_0 to p_1;
5. Condensation of dM_2, on the solution, at p_1;
6. Increase of the pressure of $M_1 + M_2 + dM_2$ from p_1 to p.

Retaining the notation of the foregoing, and denoting the specific volume and entropy of the solution by the functions

$$v(p, \theta, m_1), \qquad s(p, \theta, m_1),$$

where the quantity $m_1 = M_1/(M_1 + M_2)$ is the "composition" of the solution, the increments of the energy of the system, in the successive steps of the reversible dilution, are:

$$\delta E_1 = -\int_p^{p_1} p \frac{\partial V}{\partial p}\, dp + \theta \int_p^{p_1} \frac{\partial S}{\partial p}\, dp$$

$$\delta E_2 = \left\{ e_a(p_0, \theta) - e_a(p_1, \theta) \right\} dM_2$$

$$\delta E_3 = \left\{ -p_0 \left(v_a(p_0, \theta) - v(p_0, \theta, 0) \right) + \theta \left(s_a(p_0, \theta) - s(p_0, \theta, 0) \right) \right\} dM_2$$

$$\delta E_4 = \left\{ -\int_{p_0}^{p_1} p \frac{\partial v_a}{\partial p}\, dp + \theta \left(s_a(p_1, \theta) - s_a(p_0, \theta) \right) \right\} dM_2$$

$$\delta E_5 = \left\{ -p_1 \left(\frac{\partial V(p_1 \ldots)}{\partial M_2} - v_a(p_1, \theta) \right) + \theta \left(\frac{\partial S(p_1 \ldots)}{\partial M_2} - s_a(p_1, \theta) \right) \right\} dM_2$$

$$\delta E_6 = -\int_{p_1}^{p} p \frac{\partial V'}{\partial p}\, dp + \theta \int_{p_1}^{p} \frac{\partial S'}{\partial p}\, dp.$$

In the last of these equations, the letters V', S' denote the respective functions

$$V(p, \theta, M_1, M_2 + dM_2), \qquad S(p, \theta, M_1, M_2 + dM_2).$$

Now, before the operation, the energy of the system composed of the separate masses $M_1 + M_2$ and dM_2 is

$$E + e_2(p, \theta).dM_2;$$

after the operation, the energy of the system, now consisting of the homogeneous mass $M_1 + M_2 + dM_2$ is

$$E + e_2\, dM_2 + \Sigma\, \delta E.$$

So, during the operation the energy $E(p, \theta, M_1, M_2)$ of the solution has changed from E to

$$E + e_2 dM_2 + \Sigma\, \delta E.$$

Consequently,

$$\frac{\partial E}{\partial M_2}\, dM_2 = e_2 dM_2 + \Sigma\, \delta E.$$

We thus find

$$\frac{\partial E}{\partial M_2} = e_2(p, \theta) + \frac{1}{dM_2} \sum \delta E_i$$

$$(1) = \left\{ e_2(p, \theta) + e_2(p_0, \theta) - e_a(p, \theta) \right\}$$

$$+ \left\{ - p_0 \cdot v_a(p_0, \theta) - \int_{p_0}^{p_1} p\, \frac{\partial v_a}{\partial p}\, dp + p_1 \cdot v_a(p_1, \theta) \right\}$$

$$+ \theta \left\{ s_a(p_0, \theta) + s_a(p_1, \theta) - s_a(p_0, \theta) - s_a(p_1, \theta) \right\}$$

$$+ \left\{ p_0 \cdot v(p_0, \theta, 0) - p_1 \frac{\partial V(p_1 \ldots)}{\partial M_2} - \frac{1}{dM_2} \int_p^{p_1} p\, \frac{\partial V}{\partial p}\, dp \right.$$

$$\left. - \frac{1}{dM_2} \int_{p_1}^{p} p\, \frac{\partial V'}{\partial p}\, dp \right\}$$

$$+ \theta \left\{ - s(p_0, \theta, 0) + \frac{\partial S(p_1 \ldots)}{\partial M_2} + \frac{1}{dM_2} \int_p^{p_1} \frac{\partial S}{\partial p}\, dp \right.$$

$$\left. + \frac{1}{dM_2} \int_{p_1}^{p} \frac{\partial S'}{\partial p}\, dp \right\}.$$

From this equation, two terms in the first bracket and all the terms in the third bracket cancel.

The second bracket, when we note that

$$\int_{p_0}^{p_1} \frac{\partial p v_a}{\partial p}\, dp = \int_{p_0}^{p_1} v_a\, dp + \int_{p_0}^{p_1} p \frac{\partial v_a}{\partial p}\, dp,$$

i. e. that

$$p_1 \cdot v_a(p_1, \theta) - p_0 \cdot v_a(p_0, \theta) = -\int_{p_1}^{p_0} v_a\, dp + \int_{p_0}^{p_1} p \frac{\partial v_a}{\partial p}\, dp,$$

is seen to be equal to

$$(2) \qquad -\int_{p_1}^{p_0} v_a\, dp.$$

In reducing the fourth bracket, we have, from the definition of V′,

$$V' = V + \frac{\partial V}{\partial M_2} dM_2$$

$$\frac{\partial V'}{\partial p} = \frac{\partial V}{\partial p} + dM_2 \frac{\partial^2 V}{\partial p \partial M_2}$$

$$-\frac{1}{dM_2}\int_{p_1}^{p} p \frac{\partial V'}{\partial p}\, dp = -\frac{1}{dM_2}\int_{p_1}^{p} p \frac{\partial V}{\partial p}\, dp - \int_{p_1}^{p} p \frac{\partial^2 V}{\partial p \partial M_2}\, dp;$$

which converts the fourth bracket to

$$(3) \qquad p_0 \cdot v(p_0, \theta, 0) - p_1 \frac{\partial V(p_1 \ldots)}{\partial M_2} - \int_{p_1}^{p} p \frac{\partial^2 V}{\partial p \partial M_2}\, dp.$$

Transforming the integral in this expression by means of the relation

$$\int_{p_1}^{p} \frac{\partial}{\partial p}\left(p\,\frac{\partial V}{\partial M_1}\right) dp = \int_{p_1}^{p} \frac{\partial V}{\partial M_2}\, dp + \int_{p_1}^{p} p\,\frac{\partial^2 V}{\partial p \partial M_2}\, dp,$$

we find

$$\int_{p_1}^{p} p\,\frac{\partial^2 V}{\partial p \partial M_2}\, dp = p\,\frac{\partial V}{\partial M_2} - p_1\,\frac{\partial V(p_1\,..)}{\partial M_2} - \int_{p_1}^{p} \frac{\partial V}{\partial M_2}\, dp;$$

wherefore (3) becomes

$$p_0 \,.\, v(p_0,\, \theta,\, 0) - p_1\,\frac{\partial V(p_1\,..)}{\partial M_2} - p\,\frac{\partial V}{\partial M_2} + p_1\,\frac{\partial V(p_1\,..)}{\partial M_1} + \int_{p_1}^{p} \frac{\partial V}{\partial M_2}\, dp;$$

which may be written

$$(4) \qquad - p\,\frac{\partial V}{\partial M_2}\Bigg|_{p_0,\,0,\,0}^{p,\,\theta,\,m_1} + \int_{p_1}^{p} \frac{\partial V}{\partial M_2}\, dp.$$

In reducing the fifth bracket in like manner, we have, from the definition of S′,

$$S' = S + \frac{\partial S}{\partial M_2}\, dM_2$$

$$\frac{\partial S'}{\partial p} = \frac{\partial S}{\partial p} + dM_2\,\frac{\partial^2 S}{\partial p \partial M_2}$$

$$\frac{1}{dM_2}\int_{p_1}^{p} \frac{\partial S'}{\partial p}\, dp = \frac{1}{dM_2}\int_{p_1}^{p} \frac{\partial S}{\partial p}\, dp + \int_{p_1}^{p} \frac{\partial^2 S}{\partial p \partial M_2}\, dp;$$

which converts the fifth bracket to

$$- s(p_0,\, \theta,\, 0) + \frac{\partial S(p_1\,..)}{\partial M_2} + \int_{p_1}^{p} \frac{\partial^2 S}{\partial p \partial M_2}\, dp.$$

This expression may be written

$$-s(p_0, \theta, 0) + \frac{\partial S}{\partial M_2};$$

or

$$(5) \qquad \frac{\partial S}{\partial M_2}\Bigg|_{p_0, \theta, 0}^{p, \theta, m_1}$$

Utilizing the foregoing reductions (2), (4), (5) of the second, fourth, and fifth brackets, and noting that

$$\frac{\partial E}{\partial M_2} - e_2(p_0, \theta) = \frac{\partial E}{\partial M_2}\Bigg|_{p_0, \theta, 0}^{p, \theta, m_1},$$

our equation (1) for $\partial E/\partial M_2$ becomes

$$(6) \left[\frac{\partial E}{\partial M_2} + p\frac{\partial V}{\partial M_2} - \theta\frac{\partial S}{\partial M_2}\right]_{p_0, \theta, 0}^{p, \theta, m_1}, = -\int_{p_1}^{p_0} v_a\, dp + \int_{p_1}^{p} \frac{\partial V}{\partial M_2}\, dp.$$

From the general equation

$$dE = -p dV + \theta dS + \mu_1 dM_1 + \mu_2 dM_2,$$

we find

$$\frac{\partial E}{\partial M_2} + p\frac{\partial V}{\partial M_2} - \theta\frac{\partial S}{\partial M_2} = \mu_2;$$

whence follows that (6) may be written

$$(7) \qquad \mu_2 - h_2(p_0, \theta) = -\int_{p_1}^{p_0} v_a\, dp + \int_{p_1}^{p} \phi_2\, dp.$$

Transformation of the result

Now this result, this equation (7), is the condition of equilibrium for coexistent solution and vapor. To get it into a more familiar form, we may introduce into it the functions $\mu_2(p_1,\theta,m_1)$, $h_a(p_1,\theta)$ by means of the equations

$$\mu_2 = \mu_2 (p_1, \theta, m_1) + \int_{p_1}^{p} \phi_2 \, dp$$

$$h_2(p_0, \theta) = h_a (p_0, \theta)$$
$$= h_a (p_1, \theta) + \int_{p_1}^{p_0} v_a \, dp;$$

whereby we find the condition in its initial form

(8) $$\mu_2(p_1, \theta, m_1) = h_a (p_1, \theta).$$

That is, as asserted, the general formulation of the energy change involved in the isothermal dilution of a solution of an involatile solute through a process of reversible distillation is the condition of equilibrium for coexistent solution and vapor.

Reason for the result

It has been pointed out to me by Paul Saurel that in the analysis of the process the condition of equilibrium is introduced in the equation for the fifth step,

$$\delta E_5 = \left\{ - p_1 \left(\frac{\partial V(p_1 \ldots)}{\partial M_2} - v_a (p_1, \theta) \right) + \theta \left(\frac{\partial S(p_1 \ldots)}{\partial M_2} - s_a (p_1, \theta) \right) \right\} dM_2.$$

For, after the condensation of the vapor the energy of the system is

$$E + \frac{\partial E}{\partial M_2} dM_2;$$

before the condensation the energy is

$$E + e_a \, dM_2;$$

wherefore the change of the energy is

$$\delta E_5 = \left(\frac{\partial E}{\partial M_2} - e_a \right) dM_2;$$

whence, equating the two expressions for δE_5,

$$\frac{\partial E}{\partial M_2} + p \frac{\partial V}{\partial M_2} - \theta \frac{\partial S}{\partial M_2} = e_a + p_1 v_a - \theta s_a,$$

all at p_1, θ. This is the condition of equilibrium

$$\mu_2(p_1, \theta, m_1) = h_a (p_1, \theta).$$

Cornell University, March, 1906.

NEW BOOKS

Chemistry of the Proteids. *By Gustav Mann. Based on Professor Cohnheim's "Chemie der Eiweisskörper." Pp. xviii + 606. London: Macmillan and Co., 1906. Price: $3.25.*—The publication of Otto Cohnheim's "Chemie der Eiweisskörper" marked the beginning of a new era in our understanding of the constitution of proteid or albuminous substances. This book, bringing together, as it did, all of the accumulated data bearing on the chemical nature of proteids, and emphasizing the importance and suggestiveness of recent results, made clear in an impressive fashion the extreme complication of the chemical make-up of this most important class of substances. It became manifest that the unraveling of the chemical constitution of proteids was not to be easily accomplished, and that there remained much work to be done before chemists could expect to have a clear conception of the true nature of proteids and the chemical relationship of the different members of the group.

Since then, many able chemists have added greatly to our knowledge and additional data have rapidly accumulated, so that in the present volume Dr. Mann has had ample opportunity to bring forward a large array of new facts unknown at the time Cohnheim's book was written. Consequently, the present volume, while constructed largely upon the lines laid down by Cohnheim, is essentially a new book, presenting in orderly fashion all of the known facts—up to the date of writing—bearing upon the chemistry of proteids.

In the brief space of a review it is difficult to give an adequate conception of the breadth and true scope of the book. Mention may be made, however, of the following chapters: Reactions of Albuminous Substances, Dissociation-Products, Synthesis of Albumins, Constitution of Albumins, Physical Properties of Albumins, Classification of Albumins, etc.

In the chapter dealing with the Constitution of Albumins, we have an interesting presentation of the linking of amino-acids in the proteid molecule. The synthetic researches of Emil Fischer and Curtius have made it quite evident that the ordinary amino-acids are linked up to form neutral imino-compounds. Thus, the grouping $-CO\,|\,-NH-\underset{\dot{X}}{CH}-CO-\,|\,NH-\underset{\dot{X}}{CH}-CO-\,|\,NH-$ admits of a plausible explanation of many properties of the proteids. It makes clear why all albumins dissociate more or less uniformly even though the most diverse reagents are employed, why dissociation always takes place at certain points which may well be called the points of least resistance. Further, as our author states, it becomes plain why all albumins can be dissociated by trypsin, while each of the polysaccharides requires its own specific carbohydrate-ferment. Again, albumins in aqueous solutions are practically neutral, but have the power of combining with both acids and bases to form salts. "The amino-acids which build up the albumin molecule behave in every respect as do the albumins themselves, because the amino-acids retain their acid and basic character owing to the fact that they become linked in such a manner that the amino-radical of one molecule unites with the carboxyl-radical of another molecule," in this way preserving their double nature. The linking of the radicals which belong to the albumins is the same as in the peptids, so

carefully worked out by Emil Fischer, *viz.*, the joining of amino-acids to form imino-chains, complicated, however, by other connections within the albumin molecule.

The book is a mine of wealth in information of the chemical nature of proteids, and should be carefully read by every chemist and physiologist interested in the subject of proteid chemistry. It abounds in suggestive statements which will prove of value to the investigator, and as a reference handbook it is both accurate and complete. *Russell H. Chittenden*

Adolf von Baeyer's gesammelte Werke. *Herausgegeben zur Feier des siebzigsten Geburtstages des Autors, von seinen Schülern und Freunden. 16 × 24 cm. Vol. I: pp. cxxxii + 990; Vol. II: pp. 1194. Braunschweig: Friedrich Vieweg und Sohn, 1905. Price: paper, both volumes, 16 marks.*—This is a reprint of 278 articles by Prof. von Baeyer and by others working under his direction, originally published in the chemical journals between 1857 and 1905.

The papers are arranged under 19 heads, of which the largest are: the uric acid group (123 pp.), indigo (168 pp.), phthaleins (217 pp.), hydroaromatic compounds and the constitution of benzene (490 pp.), terpenes (267 pp.), and triphenylmethane (165 pp.). There is a table of contents, a list of over 1600 "Papers from von Baeyer's Laboratories," and an alphabetical subject-index.

The importance of the results achieved by Prof. von Baeyer are acknowledged by all; but it is doubtful whether any idea of the tremendous amount of labor they cost can be gained without actually handling these 2000 pages, while the difficulty and wearing nature of much of the work—that in connection with the reduction products of the phthalic acids for instance—can best be appreciated by those who have been privileged to enter the private laboratory at Munich.

Prefaced to the papers is a sketch of the author's life, written by himself, in which reminiscences of Bunsen and Kekulé are followed by an account of his own first laboratory in Berlin, and of how, after seeing others promoted over his head, he was finally called to Strassburg at the close of the Franco-Prussian war, and three years later took Liebig's place at Munich. These "recollections" are interesting because they trace the origins of Baeyer's great series of researches, but they lack the element of scandal. No polemical matter is introduced, even Kolbe's famous attacks are passed over in silence; in fact the only event in a long life that seems still to awake resentment in the author's breast is the failure of the Berlin examiners in 1857 to give his thesis a "first."

With its large pages and clear type, the book is a worthy monument to a life spent in continuous and successful work. Its surprisingly low price puts it within the reach of all who care for organic chemistry; and the careful arrangement of the contents makes it a real pleasure to read paper after paper, and trace the growth of ideas that have made the author famous.

W. Lash Miller

Physikalische Krystallographie *und Einleitung in die krystallographische Kenntnis der wichtigsten Substanzen. By P. Groth. Vierte, neubearbeitete Auflage. 18 × 25 cm; pp. xiv + 820. Leipzig: Wilhelm Engelmann, 1905. Price: paper, 19 marks, bound, 22 marks.*—The appearance of this edition of

Groth's Physical Crystallography should attract the attention of all scientific men who have to do with crystallized matter, since it is the fruit of a lifetime devoted to teaching crystallography. In general purpose and arrangement the book remains the same as in the preceding edition of 1895, though a large number of changes, some of them quite extensive, have been made in subordinate details. These changes, in the main, are designed to secure didactic unity and clearness, also to embody the results of recent research.

The three principal divisions of the book are: I. General Physical Crystallography, The Properties of Crystals; II. Special Physical Crystallography, Systematic Description of Crystals; III. Applied Physical Crystallography, Methods of Investigating Crystals.

Many readers of this journal will be especially interested in the announcement, casually made in the preface, that the author's complete Handbook of Chemical Crystallography will shortly begin to appear. *A. C. Gill*

Lehrbuch der physikalischen Chemie *für technische Chemiker und zum Gebrauche an technischen Hochschulen und Bergakademien. By Hanns v. Jüptner. 15 × 23 cm. I. Teil, Materie und Energie, pp. 194, 1904. II. Teil, Chemisches Gleichgewicht und Reaktionsgeschwindigkeit: Erste Hälfte, Homogene Systeme, 1904; Zweite Hälfte, Heterogene Systeme, 1905; pp. 358. Leipzig und Wien: Franz Deuticke. Price, paper: I, 4.00 marks; II, erste Hälfte, 3.50 marks; zweite Hälfte, 4.50 marks.*—According to the preface, this work is published on account of the importance of physical chemistry in technical work, and aims to present chiefly what may prove useful technically. The work is to form a kind of introduction to a *Lehrbuch* of chemical technology which the author has undertaken. The first part, matter and energy, is devoted to such general subjects as states of aggregation, heat and energy relations, thermodynamics and theories of solution—22 chapters. Each chapter consists of a short summary of generally accepted views upon a particular subject. Most of these views can be found in Nernst's *Theoretische Chemie* or Ostwald's *Grundriss*. The treatment is not as complete as Nernst, because the ideal laws of dilute solutions are given as apparently sufficient for all cases. The author formulates how an increase of internal energy consists partly of an increase of kinetic motion (rise of temperature) and partly of displacements against internal forces (internal work).

Before treating equilibrium, a good statement of various ways of expressing concentration is given. This would aid one in reading papers containing various units, etc. In the twenty-nine following chapters, homogeneous equilibrium is first considered; then heterogeneous, and the velocity of reaction is treated last under each case. This part follows van 't Hoff. A great many examples are given with numerical data, graphic representation of phase relations, and good explanations. These constitute a good selection from various journals of physical chemistry. References are usually given. Finally, special technical processes are considered, showing practical applications of the principles developed.

The treatment of hydrolysis is unsatisfactory. When a salt is *vollständig gespalten* it is hard to see how $C_{SH} = C_S = C_B$ and $C_S \times C_B$ surely becomes $(C_S)^2$ not $2C_S$ (p. 82). The nomenclature and symbols are a fair selection from

various schools; but $Cu^{+''}$ and $PO_4^{-'''}$ seem more awkward than $Cu^{''}$ and $PO_4^{'''}$. The mass-law is overapplied, at least in the case of solutions, where relations are assumed to be much simpler than they really are.

The book is a concise summary, such as technical chemists usually wish. It covers a lot of ground. It is not suggestive but rather didactive in spirit. Theories are presented along with facts, with no attempt to show the relations between facts and one or more hypotheses. There is very little electrochemistry. In fact no specialist would be content with any particular subject treated. Apparatus and methods of experimentation are mentioned only incidentally.

Roger Clark Wells

REVIEWS

The object of this department of the Journal is to issue, as promptly as possible, critical digests of all Journal articles that bear upon any phase of Physical Chemistry.

General

The true atomic weight of nitrogen. *G. Hinrichs. Comptes rendus*, 140, *1590* (*1905*).—A discussion of the atomic weight of nitrogen. The author believes that the true value is 14.000. It must be admitted that the developments of the last few years have been bringing the experimental values of the atomic weights nearer to those assigned years ago by Hinrichs. *W. D. B.*

Compressibility of different gases under less than one atmosphere, and the determination of their molecular weights. *G. Lemoine. Comptes rendus*, 140, *1384* (*1905*).—The author has determined the compressibility at 0° of hydrogen, oxygen, nitric oxide, ammonia and sulphur dioxide between 400 mm and 800 mm; and of ammonia and sulphur dioxide between 200 mm and 400 mm. The values of the atomic weights, as calculated from the densities, agree with the gravimetric determinations except in the case of nitrogen. *W. D. B.*

Atomic weight of nitrogen deduced from the ratio of the densities of nitrogen and oxygen. *P. A. Guye. Comptes rendus*, 140, *1386* (*1905*).—Six methods of calculating the atomic weight of nitrogen from its density give 14.009 as a mean value. *W. D. B.*

Expansion and density of some gases at high temperatures. *A. Jaquerod and F. L. Perrot. Comptes rendus*, 140, *1542* (*1905*).—The authors have determined the coefficients of expansion for nitrogen, air, oxygen, carbon monoxide and carbon dioxide between 0° and 1067°. From the data the authors calculate the following molecular weights: nitrogen, 28.0155; carbon monoxide, 28.009; carbon dioxide, 43.992. *W. D. B.*

Density of nitric oxide. *P. A. Guye and C. Davila. Comptes rendus*, 141, *826* (*1905*).—The weight of a normal liter of nitric oxide is 1.3402. From this the authors deduce a value of 14.006 from the atomic weight of nitrogen. *W. D. B.*

Densities of carbon dioxide, ammonia and nitrous oxide. *P. A. Guye and A. Pintza. Comptes rendus*, 141, *51* (*1905*).—The authors obtain densities of 1.9768, 0.7708 and 1.9774 for CO_2, NH_3 and N_2O, respectively, at pressures of 0.1 atm. The atomic weight for nitrogen becomes 14.007, 14.006 or 14.009 if deduced from the ratios $N_2O : CO_2$, $N_2 : CO$ or $N_2 : O_2$. *W. D. B.*

Extraction of terbium. *G. Urbain. Comptes rendus*, 141, *521* (*1905*).—Terbium has been prepared by fractional crystallization of the double nitrate with nickel; of the nitrate in presence of bismuth nitrate; and of the ethyl sul-

phates. The absorption spectrum of the neutral chloride has been determined. A value of 159.2 was obtained for the atomic weight. *W. D. B.*

Victorium and the ultra-violet phosphorescence of gadolinium. *G. Urbain. Comptes rendus*, 141, *954* (*1905*).—Gadolinium shows the same ultra-violet phosphorescent spectrum as victorium and it is therefore believed that this latter element is non-existent. *W. D. B.*

Dense liquids. *Duboin. Comptes rendus*, 141, *385* (*1905*).—Thoulet's solution contains potassium and mercuric iodides and has a density of 3.2. When sodium is substituted for potassium, a liquid is obtained having a density of 3.46. This liquid dissolves without change in a number of organic liquids, such as alcohols, aldehydes, acids, esters and acetone. It causes cellulose to swell in a surprising manner. *W. D. B.*

Thermochemistry of neodymium. *C. Matignon. Comptes rendus*, 141, *53* (*1905*).—Experiments on the heats of formation and the heats of solution of neodymium salts show that these substances belong thermochemically between the magnesium salts and those of the alkaline earths. *W. D. B.*

Combustion of sulphur in the calorimetric bomb. *H. Giran. Comptes rendus*, 140, *1904* (*1905*).—The formation of solid S_2O_7 from solid SO_3 and oxygen is accompanied by an absorption of 9710 cal., while the heat evolved, when solid S_2O_7 is dissolved in much water, is 56710 cal. The presence of hydrogen in the compressed oxygen may introduce serious and unexpected errors. *W. D. B.*

Methods of measuring heats of combustion of organic compounds. *M. Berthelot. Comptes rendus*, 140, *1497* (*1905*).—A reply to Thomsen (9, *711*). *W. D. B.*

One-Component Systems

Some physical properties of propane. *P. Lebeau. Comptes rendus*, 140, *1454* (*1905*).—Pure propane boils at —44.5°; its critical temperature is 97.5°, and its critical pressure 45 atm. Both ethane and propane are still liquid at —195°. Propane is more soluble in many liquids than either ethane or methane. *W. D. B.*

Mechanical properties of crystallized iron. *F. Osmond and C. Frémont. Comptes rendus*, 141, *361* (*1905*).—The authors were able to obtain samples of a steel rail from which they could extract large crystals of practically pure iron. It was found that this iron broke readily along the cleavage planes, but that it showed marked plasticity in all other directions. *W. D. B.*

Distillation of copper. *H. Moissan. Comptes rendus*, 141, *853* (*1905*).—With a 300 ampere, 110 volt arc, fifty grams of copper can be distilled in five minutes. It seems to the reviewer that a resistance furnace would be much more satisfactory. *W. D. B.*

Two-Component Systems

Constitution of the copper-aluminum alloys. *L. Guillet. Comptes rendus*, 141, *464* (*1905*).—The author believes that the following phases occur in the copper-aluminum series: α, a solid solution containing 0–10 percent aluminum;

β, probably the compound Cu_3Al; γ, a solid solution stable at higher temperatures only; δ, a solid solution containing 14–30 percent aluminum; ϵ, a solid solution containing 44–46 percent aluminum; η, the compound Al_2Cu; H, either pure aluminum or aluminum containing only a small amount of copper. *W. D. B.*

Equilibrium diagram for the carbon steels. *G. Charpy. Comptes rendus*, 141, *948* (*1905*).—Steels containing less than two percent carbon show no graphite when cooled slowly from the melt. A steel containing 2.9 percent carbon shows no graphite if cooled rapidly but up to 2.2 percent graphite if cooled very slowly. [These two sentences are inconsistent.] The eutectic for graphite and solid solution is put at 1160°–1165° while the eutectic for cementite and solid solution is put at 1150°. *W. D. B.*

Fusibility of mixtures of antimony sulphide with cuprous and mercuric sulphides. *H. Pélabon. Comptes rendus*, 140, *1389* (*1905*).—The freezing-point curve for antimony sulphide and cuprous sulphide appears to consist of two branches with a eutectic of 498°. No attempt was made to determine the nature of the solid phases. With antimony sulphide and mercuric sulphide there is a eutectic at 455°. The complete curve could not be determined owing to the volatility of mercuric sulphide. *W. D. B.*

Bromine trifluoride. *P. Lebeau. Comptes rendus*, 141, *1018* (*1905*).—Fluorine and bromine combine, forming the compound BrF^3, a substance which melts at about 4°. *W. D. B.*

The state of matter near the critical point. *G. Bertrand and J. Lecambe. Comptes rendus*, 141, *320* (*1905*).—A little below a certain temperature a tube containing alcohol and alizarine shows a red liquid layer and a practically colorless gaseous layer. At a little higher temperature the contents of the tube become homogeneous and the color is uniformly distributed. The authors take this to mean that particles of liquid exist above the critical temperature. If this were so the alizarine should precipitate if the solution were heated to a still higher temperature. *W. D. B.*

The state of matter near the critical point. *C. Raveau. Comptes rendus*, 141, *348* (*1905*).—A criticism of the conclusions of Bertrand and Lecambe (preceding review). *W. D. B.*

Distillation of gold and its alloys. *H. Moissan. Comptes rendus*, 141, *977* (*1905*).—In an arc furnace the author has distilled gold. From a gold-copper alloy, copper distils faster than the gold. Tin is only slightly more volatile than gold. The material which condenses during the distillation of a gold-tin alloy has the properties of the purple of Cassius. *W. D. B.*

New preparation of rubidium and caesium. *L. Hackspill. Comptes rendus*, 141, *106* (*1905*).—The chlorides of rubidium, caesium and lithium are readily reduced by metallic calcium. It is possible to distil off the rubidium or the caesium; but with lithium an alloy of calcium and lithium is obtained. *W. D. B.*

Oxidation of powdered aluminum. *Kohn-Abrest. Comptes rendus*, 141, *323* (*1905*).—If powdered aluminum be heated in a porcelain crucible for ten

minutes to a temperature of 625°–750° in an electric furnace, the mass becomes grayish blue and the amount of oxygen taken up corresponds pretty closely to that required for the formula AlO. *W. D. B.*

The reduction of thorium oxide by amorphous boron. *Binet de Jassoneix. Comptes rendus*, 141, *191* (*1905*).—When borium and thorium oxide are heated together in an electric furnace, two borides of thorium are formed ThB_4 and ThB_6. *W. D. B.*

Action of silicon on pure aluminum. *E. Vigouroux. Comptes rendus*, 141, *951* (*1905*).—It is believed that silicon and aluminum form no compounds. In presence of a third metal, alumino silicides of the third metal may be formed. No proof is offered for either of these statements. *W. D. B.*

Multi-Component Systems

Constitution and properties of aluminum steels. *L. Guillet. Comptes rendus*, 141, *35* (*1905*).—The physical properties of steel are changed but slightly by addition of aluminum up to three percent. When over seven percent of aluminum is present the steel becomes very brittle. The micrographic examination brought out nothing positive except that aluminum decreases the solubility of carbon in iron. *W. D. B.*

Classification and comparison of ternary steels. *L. Guillet. Comptes rendus*, 141, *107* (*1905*).—The author distinguishes five classes of carbon steels containing a third component, those showing pearlite, martensite, γ-iron, carbide and graphite. The author believes that he has shown the great importance of the micrographical study of the steels as at present carried on. To the reviewer it seems that an exhaustive study of the carbon steels is more desirable at present than a superficial examination of a number of more complicated alloys. *W. D. B.*

Constitution and properties of steels containing tin, titanium or cobalt. *L. Guillet. Comptes rendus*, 140, *1689* (*1905*).—Steels containing tin, titanium or cobalt have been examined under the microscope and have been tested for tensile strength. No especial results were obtained. *W. D. B.*

Equilibrium between acetone and hydroxylamine hydrochloride. *P. Landrieu. Comptes rendus*, 140, *1392* (*1905*).—The author shows that a mass law equation represents fairly well the reversible equilibrium between the system, acetone plus hydroxylamine hydrochloride, and the system, oxime hydrochloride and water. *W. D. B.*

Action of fluorine on the oxides of nitrogen. *H. Moissan and P. Lebeau. Comptes rendus*, 140, *1573* (*1905*).—At ordinary temperatures fluorine does not react with nitrogen peroxide or with nitrous oxide. It does react with nitric oxide, the reaction at low temperatures being represented by the equation $2NO + F = NO_2F + N$. *W. D. B.*

Action of silicon chloride on iron. *E. Vigouroux. Comptes rendus*, 141, *828* (*1905*).—Below red heat iron reacts with silicon tetrachloride, forming Fe_2Si and ferrous chloride. *W. D. B.*

Preparation of binary metallic compounds by means of aluminum. *A. Colani.*

Comptes rendus, 141, *33* (*1905*).—The author has prepared a number of compounds by reducing with aluminum the mixture of a metalloid or an oxide of a metalloid with an oxide of a metal. *W. D. B.*

Preparation of binary metallic compounds by means of aluminum. *C. Matignon and R. Trannoy. Comptes rendus*, 141, *190* (*1905*).—The authors have prepared phosphides, arsenides, silicides and borides by methods somewhat similar to those of Colani (preceding review). *W. D. B.*

A sub-iodide of phosphorus. *R. Bouloch. Comptes rendus*, 141, *256* (*1905*).—If a solution of phosphorus and a little iodine in carbon bisulphide be exposed to sunlight, there precipitates an amorphous red powder, P_4I. It is believed that the catalytic action of iodine on phosphorus is represented by the following equations:

$$7P \text{ (white)} + PI_3 = 2P_4I$$
$$2P_4I = PI_3 + 7P \text{ (red)}.$$

Some red phosphorus has a density intermediate between that of white phosphorus and PI_3 the first reaction, and consequently the second, could not take place in a vertical tube. *W. D. B.*

Decomposition of ammonium sulphate by hot sulphuric acid in presence of platinum. *M. Delépine. Comptes rendus*, 141, *886* (*1905*).—If a solution of ammonium sulphate and sulphuric acid be boiled in presence of platinum black, nitrogen is evolved. The author believes that the platinum is dissolved by the sulphuric acid and reduced by the ammonium sulphate. *W. D. B.*

Hydrogenization of ketoximes. *A. Mailhe. Comptes rendus*, 141, *113* (*1905*).—If hydrogen and acetoxime are passed over pulverulent nickel, heated to 150°-180°, they are converted into propylamine and diisopropylamine. This is an excellent method for preparing the secondary amines. *W. D. B.*

Hydrated ferric sulphate. *A. Recoura. Comptes rendus*, 141, *108* (*1905*).—If a solution containing ferric sulphate be allowed to evaporate at constant temperature a basic salt precipitates first. On evaporating to complete dryness the yellow hydrated ferric sulphate is formed $Fe_2(SO_4)_3 9H_2O$. If this be redissolved in a small amount of water and allowed to evaporate from a large surface, a white salt is formed having the same composition but different properties. [Since the author has not determined what constitutes the real difference in the two cases, the work will have to be done over again.] *W. D. B.*

A property of the alloys of aluminum with tin, bismuth or magnesium. *H. Pécheux. Comptes rendus*, 140, *1535* (*1905*).—The alloys of aluminum with magnesium or tin decompose water. Both these alloys, as well as the aluminum-bismuth alloys react with copper sulphate solution, precipitating copper and setting free hydrogen. *W. D. B.*

Effect of electrolytes on the mutual precipitation of colloids with opposite electrical charges. *Larguier de Bancels. Comptes rendus*, 140, *1647* (*1905*).—If two electrically opposed colloids be mixed in proper proportions, the mutual precipitation is complete. The addition of an electrolyte, which can precipitate one of the colloids, tends to keep the other in solution. *W. D. B.*

Osmotic Pressure and Diffusion

Permeability of glass vessels. *M. Berthelot. Comptes rendus*, 140, *1286* (*1905*).—Ordinary glass is readily permeable to hydrogen above 550°, to nitrogen at 600° and to oxygen or carbon monoxide at 650°. No hydrogen passes through Jena glass at 700° but diffusion occurs at 750°–775°. Oxygen does not diffuse until the temperature exceeds 800°. *W. D. B.*

Velocities

Rate of crystallization of supersaturated solutions. *C. Leenhardt. Comptes rendus*, 141, *188* (*1905*).—Crystallized sodium acetate melts at 58°. Between 58° and 25° supercooling increases the rate of crystallization. From 23° to —20° the rate is practically constant while at —40° the rate of crystallization is practically zero. The constant rate is independent of the diameter of the tube. *W. D. B.*

Electromotive Forces

Thermoelectric force and the Thomson effect. *A. Ponsot. Comptes rendus*, 140, *1585* (*1905*).—The author deduces a relation between the coefficient of the Thomson effect and the thermo-electric series which holds for a temperature below that of the lowest neutral point in a series of metals. The relation does not hold actually for all known cases. *W. D. B.*

Electrolysis and Electrolytic Dissociation

Molecular heats of strong and weak electrolytes. *P. T. Muller and C. Fuchs. Comptes rendus*, 140, *1639* (*1905*).—The apparent molecular heat of the salt in a solution of a strong electrolyte varies with the composition while this is not the case with weak electrolytes. The author adopts the hypothesis of hydrated ions as an explanation. *W. D. B.*

The specific heats of copper sulphate solutions. *P. Vaillant. Comptes rendus*, 141, *658* (*1905*).—The solutions were heated by an incandescent lamp instead of by a wire. The actual specific heat decreases with increasing concentration. If one calculates the hypothetical specific heat of dissolved $CuSO_4 5H_2O$, the value is found to pass through a maximum with increasing concentration. *W. D. B.*

Dielectricity and Optics

Specific inductive capacity of benzene and water. *F. Beaulard. Comptes rendus*, 141, *656* (*1905*).—With a wave-length of 50 m the author finds a dielectric constant for thiophene-free benzene lying between 1.615 and 1.700. For water a value of 11.04 was obtained, which differs enormously from the usual value of eighty odd. *W. D. B.*

Experiments on liquid dielectrics. *P. Gouré de Villemontée. Comptes rendus*, 141, *179* (*1905*).—The propagation of electrical charges through petroleum or paraffin oil is comparable to the values found for crystals by Curie. *W. D. B.*

A GENERAL METHOD OF CALCULATION IN KINETICS: THE METHOD OF AREAS. A METHOD OF APPROXIMATE EFFECTIVE AVERAGES.

BY RALPH E. DE LURY

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PART I. THEORETICAL.

Introduction

In recent investigations in Chemical Kinetics there occur differential relations of the type,

$$\frac{dx}{dt} = K(A - x)^l\ (B - x)^m(C - x)^n \qquad (1)$$

where l, m, n, are positive or negative, and generally, though not always, integral. The problem is, in any case, to discover

values of K, l, m, n that suit the particular reaction. The method of solving it, is to assume values of l, m, n, and then to examine whether for different values of t and the corresponding values of x the value of K is constant. But to do this we need the integral of the equation (1), and this integral can seldom be found in a form that lends itself to ready computation. In such cases methods of approximation have been employed. A short discussion of these methods will first be given, and this will be followed by an account of a method which, though implying in the end a mechanical quadrature, is on its theoretical side, rigorous. Further, the area as found by the planimeter or other means, represents a degree of accuracy quite as high as the experimental data warrant.

Methods that have been used

(I) *Integration by Partial Fractions*

In equation (1) assume l, m, n, to be positive integers; then,

$$K\int_0^t dt = \int_0^x \frac{dx}{(A-x)^l(B-x)^m(C-x)^n}. \qquad (2)$$

Therefore,

$$Kt = \int_0^x \left[\sum_{r=1}^{r=l}\frac{L_r}{(A-x)^r} + \sum_{r=1}^{r=m}\frac{M_r}{(B-x)^r} + \sum_{r=1}^{r=n}\frac{N_r}{(C-x)^r}\right]dx. \quad (3)$$

The integration yields $l + m + n - 3$ terms of the type,

$$-\frac{L_r}{r-1}\cdot\frac{1}{(A-x)^{r-1}}$$

and 3 terms such as,

$$L_1 . \log_e (A-x),$$

where L_r, M_r, N_r are functions of A, B, C, which can be determined, and hence K can be calculated.

When certain of the exponents l, m, n are negative the integral is evaluated in a somewhat similar manner.

This method is the one commonly employed and it im-

plies that l, m, n are integers. The calculation is complicated when some or any of the positive exponents are at all large. For the case, $l = m = n = 1$, the values are easily found.[1]

(II) *Integration by Series*

Equation (2) may be written,

$$KA'B^mC^n\int_o^t dt = \int_o^x \left(1-\frac{x}{A}\right)^{-l}\left(1-\frac{x}{B}\right)^{-m}\left(1-\frac{x}{C}\right)^{-n} dx \qquad (4)$$

$$= \int_o^x \left[1 + x\left(\frac{l}{A}+\frac{m}{B}+\frac{n}{C}\right) + x^2\left(\frac{l(l+1)}{2A^2}+\frac{lm}{AB}+..\right)+..\right]dx.$$

Therefore,

$$R = \frac{x}{t}\left[1+\frac{x}{2}\left(\frac{l}{A}+\frac{m}{B}+\frac{n}{C}\right)+\frac{x^2}{3}\left(\frac{l(l+1)}{2A^2}+\frac{lm}{AB}+..\right)+..\right] \qquad (5)$$

where $R = K A' B^m C^n$, that is, the initial rate.

This series is only rapidly convergent when the ratios, $\frac{x}{A}, \frac{x}{B}, \frac{x}{C}$, are small, and the calculation becomes tedious for values of these ratios greater than about one-fourth.

This method was used in calculating the values of R in the measurements of the rate of oxidation of potassium iodide by chromic acid.[2] The values of R are very close approximations. In the case where x was greatest (12 percent of the least concentration, A), an error of only 1 percent was made by neglecting the fourth term of the series in (5). When the coefficients of x^2, x^3, etc. are determined for any set of initial concentrations, the calculation of R (or K) is then very easy; this is therefore a good method to employ if there are many measurements in a set of experiments of the same initial concentrations.

(III) *Integration by Exponentials*

This method was introduced by Profs. W. Lash Miller and T. R. Rosebrugh.[3]

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[1] Fuhrmann: Zeit. phys. Chem., 4, 89 (1889).

[2] De Lury: Jour. Phys. Chem., 7, 239 (1903). Expts. 15, 16, 17, 25, 26, 27.

[3] Trans. Roy. Soc. Canada, Sec. 3, 73 (1903).

Equation (1) may be transformed into

$$K_1 l = \int_x^q e^{-z} z^{-l}\, dz + r/q^3 \int_x^q e^{-z} z^{2-l}\, dz$$

$$-s/q^3 \int_x^q e^{-z} z^{3-l}\, dz, \text{ etc.,} \qquad (6)$$

where K_1, q, r, s, and z are expressible in terms of A, B, C, l, m, n, and x.

Numerical values of certain of these functions have been computed; and by means of these tables the values of K can be calculated. The method is adapted to cases in which one concentration is smaller than the others and holds for all real values of the exponents.

(IV) *Direct Use of the Differential Equation*

W. C. Bray has recently described a method for the calculation of K from the differential equation.[1]

If, for example, the rate proceed in accordance with the equation:

$$dx/dt = K(A - x)(B - x)^3 \qquad (7)$$

he calculates values of k, defined by

$$dx/dt = k(A - x)$$

from successive pairs of x and t; and from them obtains K by the relation

$$K = \frac{k_1}{(B - x_1)^3} = \frac{k_2}{(B - x_2)^3} \qquad (8)$$

from which K can be calculated.

This method is particularly good when A is small relatively to the other concentrations. When there are several concentrations of about the same magnitude, and when the exponents are high, or are not integral, or are variable, difficulties arise in the use of this method; however, it should be of service in the study of complex reactions such as that treated by Bray in the paper cited.

[1] Jour. Phys. Chem., 9, 573 (1905).

The above methods are somewhat limited in their application. The last three methods are approximate, but they will furnish for many cases approximations sufficiently close. The following method, general in its application, evades computations except those numerical reductions necessary for the construction of the curve, gives results as accurate as the results of the experiments sanction, and reveals readily the values of the exponents.

The Method of Areas[1]

(I) *General Case*

Suppose the reaction to take place according to the following equation,

$$\frac{dx}{dt} = \mathrm{K}.\mathrm{F}(x). \tag{9}$$

We have then,

$$\int_o^x dx = \mathrm{K}\int_o^x \mathrm{F}(x).dt$$

and therefore,

$$x = \mathrm{K}\int_o^x \mathrm{F}(x).dt. \tag{10}$$

If the curve $\mathrm{F}(x)$, t be plotted as in Fig. 1, where PQR is the curve $\mathrm{F}(x)$ t we have,

[1] This method suggested itself to the writer in April, 1905, while studying a case of complex oxidation: "The Rates of the Reactions in Solutions Containing Arsenious Acid, Potassium Iodide, Potassium Bichromate, and Sulphuric Acid," which is about to be published. While writing the present paper his attention was called to the article on *Mittlere Geschwindigkeit* by A. Fuhrmann (Zeit. phys. Chem., 4, 520 (1889); also, "Differential- und Integralrechnung" by the same author), who has given an excellent mathematical treatment of the subject of *average rate*. The writer knows of no instance where the ideas given in this paper have been applied in the study of Chemical Kinetics.

$$x = K\int_0^x F(x).dt$$

$$= K \times \text{area (OPQRT)}. \qquad (11)$$

By methods described below, the area (OPQRT) can be found accurately and hence the constant K can be calculated

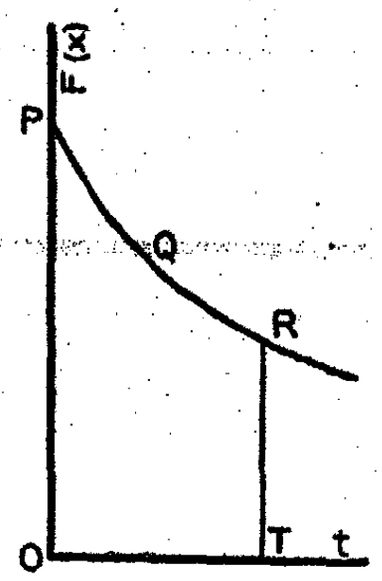


Fig. 1

for any assumed indices in the function, $F(x)$, and in this way the appropriate exponents can be determined.

Measurement of the Area

By using the experimental values of x, or preferably those taken from the x, t curve (as in Fig. 2), the function $F(x)$ can be calculated, and the curve $F(x)$, t (as in Fig. 1), can b plotted on section paper to a suitable scale (as large as possible). (*a*) The areas, $\int_0^x F(x).dt$, can then be quickly found by means of a planimeter. A good instrument will enable the operator to find the areas in question as accurately as the curve can be plotted (see Table VII, Part II). If a planimeter be not available the area may be calculated by employing certain approximate formul s for the area.

(*b*) By regarding the area as made up of a series of tra-

peziums of equal base, Δt, the area is expressed approximately thus,

$$\text{Area} = \Delta t(F_o + F_1 + F_2 + \ldots\ldots + F_n) - \Delta t.\ \frac{F_o + F_n}{2} \qquad (12)$$

where F_o, F_1, F_2, $\ldots . F_n$, are the values of $F(x)$ when $t = 0$, Δt, $2\Delta t$, $\ldots n\Delta t$. This formula is easily applied and, in general, gives close approximations without taking n very large.

(*c*) Some of "Simpson's Rules"[1] may be applied, or the squares of the section paper may be counted, or if the paper is sufficiently heavy the areas may be found by weighing.

Reverse or Successive Reactions

Suppose we have,

$$\frac{dx}{dt} = K_1.F_1(x) \pm K_2.F_2(x) \qquad (13)$$

then,

$$x = K_1\int_o^x F_1(x).dt \pm K_2\int_o^x F_2(x).dt. \qquad (14)$$

This is the general relation showing the progress of a reaction. In many cases the amount of change due to reverse or successive reactions is negligible; sometimes also there are instantaneous successive reactions: in such cases equation (10) would be used in place of equation (14). When, however, the change due to reverse or successive reactions is not negligible, by plotting $F_1(x)$ and $F_2(x)$, the values of K_1 and K_2 can be found by means of equation (14), any two experimental values of x with their corresponding measured areas being used.

Equation (14) generally takes some such form as,

$$x = K_1\int_o^x (A - x)^l(B - x)^m.dt - K_2\int_o^x (C - x)^n(D - x)^r.dt. \qquad (15)$$

[1] See Williamson's Integral Calculus, p. 212.

It may be possible to determine one of the constants by choosing conditions such that the amount of change due to the other rate is negligible.[2] In many cases, however, this is not necessary, as equation (15) is easily applied.

(II) *Special Case*: $F(x) = A - x$

Let equation (10) take the form,

$$x = K\int_0^t (A - x).dt. \qquad (16)$$

Then,

$$x = K(At - \int_0^t x.dt)$$

$$= K.\left\{\text{area (OPQT)} - \text{area (OSRT)}\right\}$$

$$= K.\ \text{area (OPQRS)} \qquad (17)$$

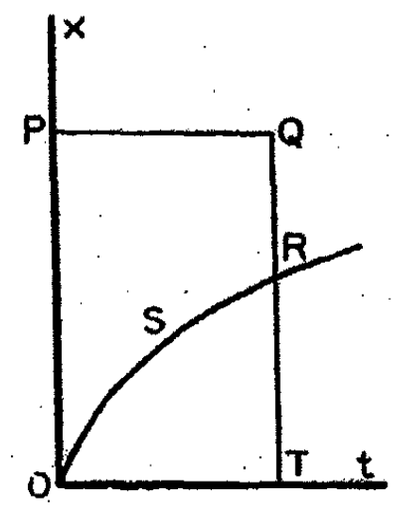


Fig. 2

where ORS is the curve x, t (Fig. 2), and OP = A.
Also,

$$\frac{x}{t} = K(A - \frac{1}{t}\int_0^t x.dt) \qquad (18)$$

where $\frac{x}{t}$ is the *average rate* during the interval $= o$ to $t = t$,

[2] As in the case of iodide oxidation by arsenic acid : See Part II, Table I, for applications to this case.

and $\frac{1}{t}\int_0^x x.dt$ is the *effective average* value of $A - x$, that is, the effective average concentration of the chemical represented by A. Writing X for the effective average value of x that is, for $\frac{1}{t}\int_0^x x.dt$, we have,

$$\frac{x}{t} = K.(A - X). \tag{19}$$

(III) *Approximate Treatment: The Method of Approximate Effective Averages*

By extending the idea of effective averages a useful approximate formula is obtained as follows: If the reaction be represented by the equation,

$$\frac{dx}{dt} = K(A - x)(B - x)^m(C - x)^n \tag{20}$$

where B and C are large relatively to A, we have as a first approximation

$$\frac{x}{t} = K(A - X)\ (B - \frac{x}{2})^m\ (C - \frac{x}{2})^n \tag{21}$$

where X, as used above, has the value $\frac{1}{t}\int_0^x x.dt$. A much closer approximation is furnished by the following equation,

$$\frac{x}{t} = K(A - X)\ (B - X)^m\ (C - X)^n \tag{22}$$

where $A - X$, $B - X$ $C - X$, are *approximate effective average concentrations*. Under certain conditions equation (22) is a very close approximation (see Tables of Part II). The smaller the value of $m + n$ the closer the approximation; it is therefore very close when some of the exponents are negative. The difference between (22) and the exact equation (10) cannot be easily expressed mathematically.

(IV) *Application of the Above Methods to the Determination of the Exponents*

(*a*) Equation (22) may be employed in the form,

$$o = \log K + \log (A - X) + m.\log (B - X) + n.\log (C - X) - \log \frac{x}{t}. \quad (23)$$

By using a sufficient number of values of x and t, the numbers K, m, n, may be calculated approximately.

(*b*) For any assumed exponents, equation (10) can be easily tested. $F(x)$ is calculated by logarithms and if these be put down systematically it will be an easy matter to calculate this function for various sets of exponents. However, the following method may be employed:

Suppose,

$$dx = K.f_1(x).f_2(x) \quad (24)$$

where $f_1(x)$ and $f_2(x)$ are functions of x. If $f_2(x)$ be plotted and $f_1(x)$ be a simple function (such as $A - x$), we have as a close approximation,

$$x = f_1(X).\int_o^x f_2(x).dt. \quad (25)$$

For example, if,

$$x = K.\int_o^x (A - x)^l (B - x)^m (C - x)^n . dt$$

we have approximately,

$$x = K.(A - X)^r \int_o^x (A - x)^{l-r} (B - x)^m (C - x)^n . dt \quad (26)$$

where r is supposed small (*e.g.*, $r = 1$). So that if the function had been plotted for the exponents $l - r$, m, n the values of $K(A - x)^r$ and hence of K can be found very closely by means of equation (26). This approximation will be of use in tracing the change in r where r is variable, as in the case of iodide oxidized by chromic acid mentioned above).

PART II. PRACTICAL APPLICATIONS

In the following applications of the foregoing principles, the curves used in measuring the areas were plotted to a suitable scale on millimeter section paper. The areas were measured by means of a planimeter, the arm being adjusted so that a reading of 1000 corresponded to 100 square centimeters. No difficulty was experienced in getting duplicate readings to agree (see Table VII). These readings were then reduced to the proper unit.

(*I*) *Mr. Roebuck's measurements on the Rates of the Reactions in Solutions containing Arsenious, Arsenic, and Sulphuric Acids, Iodine and Iodide.*[1] (Table I).

(*A*) *Comparison of Different Methods of Calculation*

This case is chosen as it affords a ready means of comparing the results of several methods of calculation, namely, the exponential method (employed by Roebuck in his original paper), Bray's method of employing the differential equation, the method of areas, and the method of approximate effective averages.

When iodide is oxidized by arsenic acid, the arsenious acid and triiodide formed react reversely. According to Roebuck, the law governing the reaction (apart from a slight deviation in the exponents of the concentrations of iodide and sulphuric acid) is as follows,

$$\frac{dx}{dt} = K_1(C-x)(D-x)(E-x) - K_2x^2(C-x)^{-3}(D-x)^{-1}, \qquad (27)$$

where x denotes the amount of triiodide, and therefore the amount of arsenious acid formed, and C, D, E denote respectively the amounts of potassium iodide, sulphuric acid and arsenic acid initially present.

For this case then, equation (14) assumes the form:

$$x = K_1\int_0^x F_1(x).dt - K_2\int_0^x F_2(x).dt$$

[1] Roebuck: Jour. Phys. Chem., 6, 365 (1902); 9, 727 (1905). See also Bray: Ibid., 9, 573 (1905).

$$= K_1 \int_0^x (C-x)(D-x)(E-x)dt$$

$$- K_2 \int_0^x x^2.(C-x)^{-2}(D-x)^{-1}dt. \quad (28)$$

In Roebuck's notation, K_1 is $k_5.V^{-3}$, and K_2 is $k_3.V$, where V is the volume in litres.

(*a*) *Assuming* $K_2 \int_0^x F_2.dt = o.$

If we neglect the second term (representing the rate of oxidation of arsenious acid by triiodide) we may calculate k_5, which will then, of course, vary (in most of Roebuck's measurements this variation is negligible), by means of the equation,

$$x = k_5 . V^{-3} . \int_0^x (C-x)(D-x)(E-x)\,dt \quad (29)$$

or approximately (see equation (22)),

$$x = k_5 . V^{-3} t\,(C-X)(D-X)(E-X) \quad (30)$$

where $X = \frac{1}{t}\int_0^x x.dt$, that is, the *effective average* value of x for the interval t.

The curves $F_1(x)$, t and x, t were plotted (as in Fig. 3), the areas, $\int_0^x F_1(x).dt$ and $\int_0^x x.dt$ measured, and the values of k_5 calculated employing equations (29) and (30). The constants thus calculated are denoted by (29),k_5 and (30),k_5 in the following table. In this table the values of t, x, and k_5 are taken directly from Roebuck's Table XXVIII. The values of (dif),k_5, that is, the constants calculated by using the differential equation (see equation (8)), are taken from Bray's Table XXVIII.

(*b*) *Assuming* $k_3 = 0.28$

The constant (31),k_5 is calculated from equation (28), assuming the value of k_3 to be 0.28 (as Bray does in calculating (dif),k_5). For making this calculation the curve $F_2(x),t$ was plotted, and from the areas measured, (31),k_5 was obtained by means of the relation,

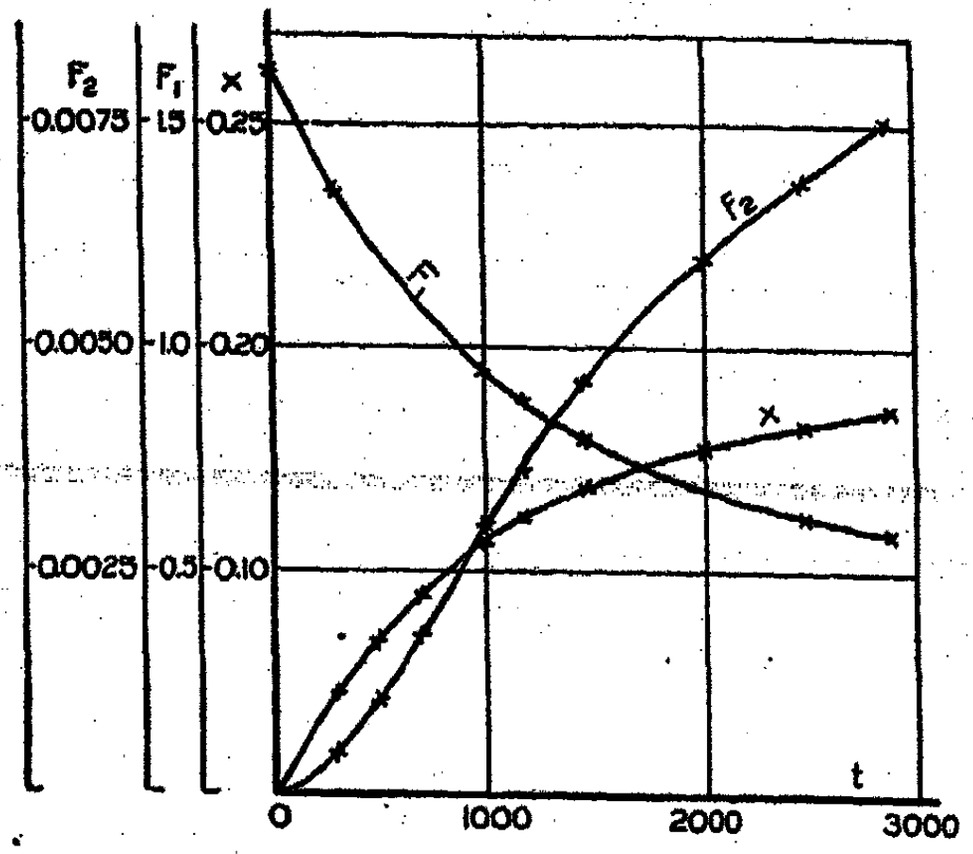


Fig. 3

$$k_5 = (29),\ k_5 \cdot \frac{x + k_3 \cdot V \cdot \int_0^x F_2(x).dt}{x} \qquad (31)$$

(*c*) *Comparison of the "Constants"*

It will be seen from Table XXVIII that (30),k_5 is practically identical with the "constant" (29),k_5, while k_5 which was calculated by the exponential method grows smaller and smaller as x increases, as would be expected. A comparison of (31),k_5 and (dif),k_5 shows the latter to be somewhat erratic. The reason that the various approximations are so close to those calculated by the area method, is that C and D are much larger (seven times) than E.

(*B*) *Calculation of* K_1 *and* K_2 *Assuming the Exponents as in Equation* (28)

K_1 and K_2 were calculated from equation (28), the two values of x necessary in each case being taken from successive measurements in Roebuck's Table XXVIII.

From these numbers the constants, $(28),k_5$ and $(28),k_3$ were calculated from the relations, $K_1 = (28), k_5.V^{-3}$ and $K_2 = (28),k_3.V$. The value of $(28),k_5$ is the same as the initial value of $(29),k_5$ in calculating which the other rate was neglected: this is natural, as of course the other rate is practically zero at the beginning of the experiment. The constant, $(28),k_3$, is found to be 0.049, that is, about one-sixth the value of k_3 (viz., 0.28) found in experiments where the concentrations were very different from those of Table XXVIII. This points to a change in the constant itself or (as Roebuck supposed) to a change in the values of the exponents, and shows that the *two* assumptions, viz., that $k_3 = 0.28$, and that the exponents are the same as in equation (28), cannot both be true for concentrations such as those used in the experiments of Roebuck's Table XXVIII. It is consequently not surprising to find that the constants $(31),k_5$ and $(dif),k_5$ rise in value—either the correction for the rate of oxidation of arsenious acid by triiodide is too great, or the exponents of the other rate are too low. It is also not surprising that $\frac{k_3}{k_5}$, calculated[1] on the above *two* assumptions, is five or six times greater than the equilibrium constant, K_6,[2] which is calculated on the one assumption. Since, moreover, the numbers, $(28),k_3$ and $(28),k_5$ (in the following Table I), are calculated on the *one* assumption that the exponents are the same as in equation (28), their quotient (the equilibrium constant) should be the same as K_6[2] of Roebuck's Table XXXIII, which was calculated on the same assumption,

[1] Roebuck: Loc. cit., p. 396, $\frac{k_3}{k_5} = \frac{0.28}{3.26 \times 10^{-7}} = 8.6 \times 10^5$, or better, $\frac{0.28}{3.7 \times 10^{-7}}$.

[2] Ibid: Table XXXIII, p. 395.

the concentrations being about the same in the two tables. Such we find to be the case, for,

$$\frac{(28),k_3}{(28),k_6} = \frac{0.049}{3.7 \times 10^{-7}} = 1.3 \times 10^5; \text{ and } K_6 = 1\ 5 \times 10^5.$$

It is probable, however, that this value of the equilibrium constant is not correct, since the exponents of the equation (28) do not hold for the concentrations of the table from which it is calculated (see Roebuck s second paper).

(*C*) *Mr. Clark's Work on the Rate of Oxidation of Iodide by Bromate in Acid Solution*

Mr. R. H. Clark gives, in a paper about to be published, the following equation to represent the rate of oxidation of iodide by bromate in acid solution,

$$\frac{dx}{dt} = K(A - x)\ (B - x)\ (C - x)^2 \qquad (32)$$

where A, B, and C denote the amounts (in equivalents) of bromate, iodide and acid respectively, initially present, and x denotes the amount (in the same unit) of iodide oxidized in t minutes. Several investigators (see the above-mentioned paper) have studied this reaction, but have not interpreted their measurements as in (32). Some of their measurements have been recalculated, employing the approximate equation (see equation (22)),

$$x = Kt(A - X)\ (B - X)\ (C - X)^2 \qquad (33)$$

and also by using the exact relation,

$$x = K.\int_0^x F(x).dt$$

$$= K\int_0^x (A - x)\ (B - x)\ (C - x)^2.dt. \qquad (34)$$

Most of the measurements (as in Tables II–VI) could not be recalculated by any of the methods of approximation described in the preceding part, and since the reaction is of the fourth

TABLE I

C, 2.270; D, 2.293; E, 0.310; V, 0.155

t	x	$k_s.10^7$	$\frac{1}{t}\int_0^x x.dt$	(30), $k_s.10^7$	$F_1(x)$	$\int_0^x F_1(x).dt$	(29), $k_s.10^7$	$F_2(x)$	$\int_0^x F_2(x).dt$	(31), $k_s.10^7$	(dif), $k_s.10^7$	K_1	(28), $k_s.10^7$	K_2	(28), k_3
296	0.434	3.62	0.024	3.74	1.339	434	3.72	0.00040	0.035	3.84	4.0	—	—	—	—
994	0.113	3.22	0.064	3.50	0.926	1214	3.47	0.00303	1.15	5.00	5.6	0.000101	3.76	0.0073	0.047
1177	0.122	3.17	0.072	3.32	0.879	1378	3.30	0.00359	1.79	5.41	4.9	0.000105	3.91	0.0081	0.052
1432	0.137	3.07	0.084	3.26	0.795	1592	3.20	0.00460	2.83	6.14	6.5	0.000095	3.53	0.0078	0.050
2480	0.164	2.61	0.112	2.64	0.614	2316	2 64	0.00684	8.92	8.89	9.7	0.000099	3.68	0.0076	0.049
2880	0.171	2.34	0.120	2.49	0.579	2562	2.49	0.00752	11.82	9.98	9.8	0.000096	3.57	0.0072	0.047
												Avg. 0.00010	3.7	0.0076	0.049

K_1 was calculated, using equation (28); then K_2 was calculated, using the average value of K_1.

Equilibrium constant $K_e = \frac{k_3}{k_5} = \frac{0.049}{3.7 \times 10^{-7}} = 1.3 \times 10^5$.

order the method of integrating by partial fractions would lead to rather involved computation.

In Tables II–VI are given recalculations of some of Magnanini's measurements (see Mr. Clark's paper for others). These tables are chosen as they afford a means of comparing the approximate equation (33) with the exact equation (34); the constants as calculated by these methods are denoted in the tables by (33), K and (34), K respectively. X is written for the effective average value of x, that is, for $\frac{1}{t}.\int_0^x x.dt$, and $F(x)$, as in (34), is written for $(A - x)\,(B - x)\,(C - x)^3$.

The fall in the constant (34),K in the earlier tables, as also the change in this "constant" from table to table, is possibly due to the fact that A, B, and C are the analytical and not the ionic concentrations.

TABLE II

A, 11.11; B, 7.41; C, 12.96; Vol. 10 cc.

t	x	$\int_0^x x dt$	X	(33),K.10^3	10^{-2}.F(x)	$10^{-3}\int_0^x F(x).dt$	(34),K.10^3
5	0.83	2.40	0.48	144	99.8	58.3	142
12	1.44	10.8	0.90	124	77.6	121	119
13	1.46	12.4	0.95	119	75.9	126	116
21	1.84	25.2	1.20	113	63.9	183	100
25	2.05	32.0	1.28	100	57.9	207	99
41	2.73	70.0	1.71	98	41.3	283	93
52	2.97	101.6	1.96	94	38.3	326	91
84	3.69	209.2	2.49	94	23.7	419	88
91	3.81	236.0	2.59	95	22.1	431	89
175	4.82	608.0	3.47	102	10.8	560	86

TABLE III

A, 11.11; B, 7.41; C, 24.07; Vol. 10 cc.

t	x	$\int_0^x x\,dt$	X	(33),K.10^7	10^{-3}.F(x)	$10^{-3}\int_0^x F(x).dt$	(34),K.10^7
2	0.82	0.88	0.44	99	477	82.5	99
3	1.05	1.68	0.56	88	367	120.5	87
9	2.35	12.40	1.38	86	339	279	84
15	3.27	29.04	1.94	89	209	384	85
17	3.38	35.52	2.09	87	141	412	81
28	4.38	78.4	2.80	90	133	519	84
31	4.50	91.7	2.96	90	77.3	540	83
35	4.68	110.3	3.15	90	73.7	557	84
40	5.10	134.6	3.36	95	66.0	593	86

TABLE IV

A, 11.11; B, 7.41; C, 35.18; Vol. 10 cc.

t	x	$\int_0^x x\,dt$	X	(33),K 10^7	10^{-3}.F(x)	$10^{-3}\int_0^x F(x).dt$	(34),K.10^7
2	1.43	1.56	0.78	88	658	169	85
6	2.98	10.84	1.61	87	373	361	83
12	4.19	32.32	2.69	84	215	523	80
17	4.93	55.4	3.26	87	140	615	80
18	5.06	60.4	3.36	87	129	630	80
20	5.28	70.4	3.52	88	111	654	81

TABLE V

A, 11.11; B, 7.41; C, 46.29; Vol. 10 cc.

t	x	$\int_0^x x\,dt$	X	(33),K.10^7	10^{-3}.F(x)	$10^{-3}\int_0^x F(x).dt$	(34),K.10^7
2	2.03	2.24	1.12	79	957	245	83
4	3.17	7.76	1.94	80	626	385	82
6	3.93	14.56	2.43	79	448	486	81
8	4.52	23.0	2.88	81	331	558	81
10	4.90	32.7	3.27	81	267	615	80
11	5.08	37.5	3.41	82	239	640	79

TABLE VI

A, 11.11; B, 7.41; C, 57.4; Vol. 10 cc.

t	x	$\int_0^x x\,dt$	X	(33),K.10^7	10^{-3}.F(x)	$10^{-3}\int_0^x F(x).dt$	(34),K.10^7
2	2.55	2.92	1.46	70	1251	379	68
4	3.94	9.56	2.78	75	711	565	70
6	4.72	18.1	3.01	74	477	675	70
7	5.15	23.2	(3.71)	(79)	368	716	72
8	5.33	28.1	3.51	77	326	743	72

In all of the above tables, it will be seen that for small values of x, the "constant" (33),K and (34),K are practically equal. As x increases, however, the former gradually grows larger than the true "constant" (34),K, showing that the approximate value of x, namely,

$$Kt(A - X)\,(B - X)\,(C - X)^2, \qquad \text{(from equation (33))}$$

gradually falls off from the true value,

$$K\int_0^x (A - x)\,(B - x)\,(C - x)^2.dt, \qquad \text{(from equation (34))}$$

as x increases. The difference between these expressions becomes less and less as C is increased, until when C becomes four or five t mes the value of A, as in Tables IV and V, the two expressions become nearly equal; this is shown by the fact that (33).K and (34),K are nearly equal in these tables. Hence in general we have as a close approximation, if $\frac{x}{A}$ be not greater than $\frac{1}{2}$,

$$x = K.\int_0^x (A - x)^2 dt = Kt(A - X)^2. \qquad (35)$$

(D) Test of the Accuracy of the Method of Areas, and the Method of Approximate Effective Averages

The approximation (35) may be tested by assuming values of K,A,x, and the consequent values of t, and constructing

the two necessary curves: assuming K = 1, A = 10, and for x the values 1, 2, 3, 4, 5, 6, the values of t (from the equation $t = \frac{1}{10-x} - \frac{1}{10}$) become $\frac{1}{90}, \frac{2}{80}, \frac{3}{70}, \frac{4}{60}, \frac{5}{50}, \frac{6}{40}$, respectively. With these values of x and t, the curves x, t and $(A-x)^2, t$ were plotted and the two expressions for x in equation (35) were calculated from the measurements of the areas $\int_0^x x.dt$ and $\int_0^x (A-x)^2.d$ as made by the planimeter. Under the word "Reading" are given duplicate readings of the planimeter for the areas in question (Table VI), and X has its former meaning, namely, $\frac{1}{t}.\int_0^x x.dt$. The areas are expressed in the proper unit.

TABLE VII

t	x	Reading	$\int_0^x x dt$	X	$t(10-X)^2$	Reading	$\int_0^x (10-x)^2 dt$
0.0111	1.00	23; 23	0.00575	0.518	1.00	397; 396	0.99
0.0250	2.00	104; 103	0.0260	1.04	2.01	801; 802	2.00
0.0428	3.00	284; 283	0.0707	1.65	2.98	1198; 1199	3.00
0.0667	4.00	624; 626	0.156	2.34	3.91	1605; 1606	4.01
0.1000	5.00	1224; 1226	0.306	3.06	4.82	2005; 2005	5.01
0.1500	6.00	2332; 2330	0.583	3.89	5.60	2404; 2401	6.00

A comparison of the duplicate readings shows how closely areas can be measured by means of the planimeter: it is evident that these measurements can be made far more closely than a chemical analysis is usually made. Since x and $\int_0^x (10-x)^2.dt$ are identical, the exactness of the method of areas can not be doubted. The value of the approximation,

$t(10 - X)^3$, differs from x by less than 4 percent when x is 5. It is evident from this, that equation (19) is applicable to the first half of bi-molecular reactions (and consequently to reactions of a higher order when all the concentrations but two, linearly involved, are practically non-variant). Hence in such cases equations (20) and (23) may be employed to calculate the values of the constant and the exponents, and where a deviation occurs in an exponent, to trace this variation. If desirable, a correction can be made by estimating the percentage error.

The above examples are sufficient to show the applicability of the Method of Areas and the Method of Approximate Effective Averages. At present I am employing these methods in the study of some cases of complex oxidation, and also in the recalculation of some kinetic measurements which have appeared in the chemical journals.

Summary

I. An outline of the methods that have been used in the computations occurring in the study of Chemical Kinetics, is given.

II. A "*Method of Areas*" is described. The Kinetic Equation is used in the following form,

$$x = K.\int_0^x F(x).dt$$

and in the case of reverse or successive reactions, in the form,

$$x = K_1.\int_0^x F_1(x).dt \pm K_2.\int_0^x F_2(x).dt.$$

The curve $F(x)$, t is plotted, the areas $\int_0^x F(x).dt$ are then measured by means of a planimeter, and the values of K are calculated from the values of x, and thus the correctness of

the assumed function, $F(x)$, is tested. The areas can be measured as accurately as the experimental data will warrant.

III. A "*Method of Approximate Effective Averages*" is described. The Kinetic Equation is used in the form,

$$\frac{x}{t} = K\left(A - \frac{1}{t}\int_0^x x.dt\right)^l\left(B - \frac{1}{t}\int_0^x x.dt\right)^m,$$

which is a close approximation under certain conditions. This equation may be used in the following form to calculate approximately the values of K, l, m,.. by taking a sufficient number of values of x,

$$o = \log K - l.\log\left(A - \frac{1}{t}\int_0^x x.dt\right) - m.\log\left(B - \frac{1}{t}\int_0^x x.dt\right) - .. - \log\frac{x}{t}.$$

The following equation may be used in some cases in tracing the variation in an exponent (r varying),

$$x = K\left(A - \frac{1}{t}\int_0^x x dt\right)^r \int_0^x (A - x)^{l-r}(B - x)^m .. dt.$$

IV. Some examples showing the applicability and accuracy of the above methods are given.

I am glad of this opportunity of expressing my gratitude to Professor W. Lash Miller. Without the training and help I have received from him, the above problems would doubtless never have occurred to me.

University of Toronto,
March, 1906

STUDIES IN VAPOR COMPOSITION, IV

BY H. R. CARVETH AND J. P. MAGNUSSON

The necessity for accurate determinations of the boiling-point of solvents and solutions has produced many forms of apparatus designed to serve this end; students working in this laboratory have experimented with many of the variations proposed, and their criticisms have led to the adoption of a modification which has overcome some of the objections raised against other forms.

When, from the rise of the boiling-point of the solvent caused by the addition of a known amount of the solute, the molecular weight of the solute is calculated, the observer may wish to keep his experimental error below one percent; this is rarely the case, however, and for most work an error of five percent or more is allowable. The apparatus described in this paper seems suited for the measurements ordinarily required in the laboratory, while a few precautions will allow its use in cases where greater accuracy is required.

The first form proposed for work of this kind was devised by Beckmann.[1] This was a large test-tube with three necks, one carrying the special thermometer, the second the return condenser, while the third served to introduce the solute. Garnets or pieces of metal were employed to insure steady boiling. In the use of this apparatus it was found almost impossible to avoid superheating; to obtain a constant reading on the thermometer takes considerable time. By regulating the flame, however, so that the drip back is practically constant, steady conditions are realized.

This form Beckmann[2] improved by jacketing the boiling-tube with the boiling solvent, the object being to prevent radiation from the solution; in a later paper,[3] the jacket is made much simpler, and the errors inherent to the method are also

[1] Zeit. phys. Chem., 4, 544 (1889).
[2] Ibid., 8, 223 (1891); 15, 656 (1894); 21, 245 (1896).
[3] Beckmann: Ibid., 40, 129 (1903).

discussed. The time required for the determination was also reduced very materially. The first Beckmann forms were open to the objection that the cold condensate dropped back into the solution. Hite[1] and later Jones[2] have avoided this by surrounding the thermometer with a jacket of glass or platinum; drops of condensed liquid are returned to the solution surrounding the jacket. An objection to this form is, of course, that the concentration in the inner and outer layers will be different.

A new method for heating was proposed by Sakurai.[3] His apparatus consisted of a boiling flask containing a solvent, the vapor from which passed into the solution, and raised the latter to its boiling-point. The solution was held in a U-tube, one arm of which carried the vapor delivery tube, the other the thermometer. The rapidity with which the boiling-point was reached, and its constancy indicated that the new method should prove very serviceable. To this particular form of apparatus, however, there is the objection that the vapor which is passed in condenses and consequently changes the concentration of the solution. For this reason Sakurai found it necessary to redetermine the concentration after each observation.

By substituting a large test-tube for the U-tube and by jacketing the solution with the vapor from the solvent, Landsberger[4] was able to reduce very considerably the amount of condensation. Walker and Lumsden[5] then suggested that the inner tube be calibrated; this enabled the observer to read the volume of the solution and thus obviated the necessity of weighing after each observation. McCoy[6] effected a very decided improvement when he employed his boiling-flask as a jacket for the

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[1] Am. Chem. Jour., 17, 514 (1895).
[2] Ibid., 19, 581 (1897).
[3] Jour. Chem. Soc., 61, 989 (1892).
[4] Ber. chem. Ges., Berlin, 31, 458 (1898); Zeit. anorg. Chem., 17, 422 (1898).
[5] Jour. Chem. Soc., 73, 502 (1898).
[6] Am. Chem. Jour., 23, 353 (1900).

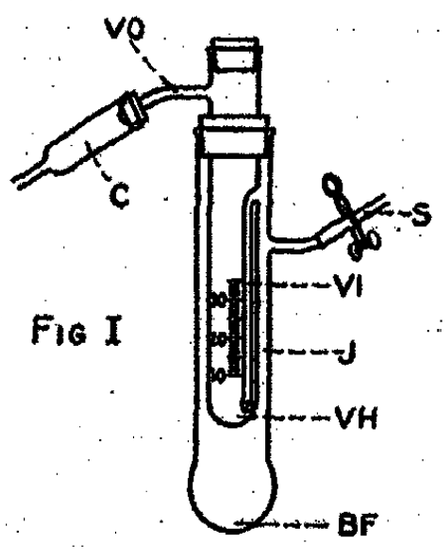


FIG I

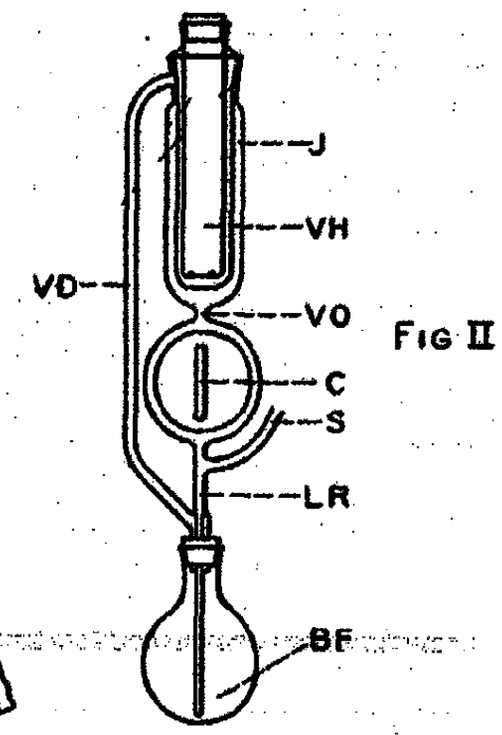


FIG II

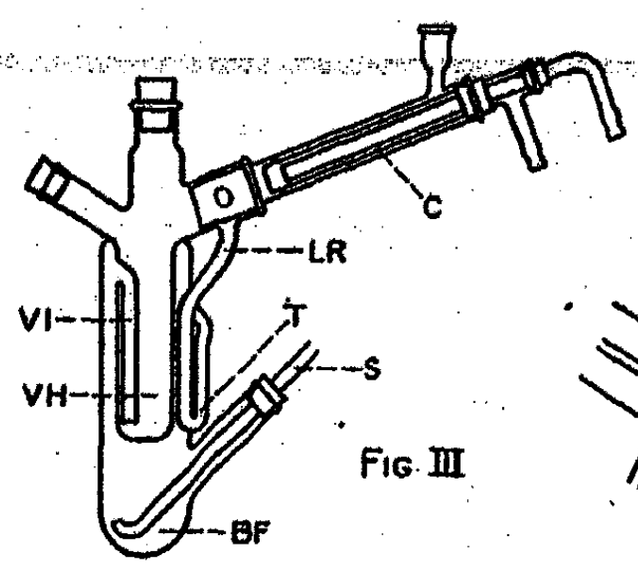


FIG III

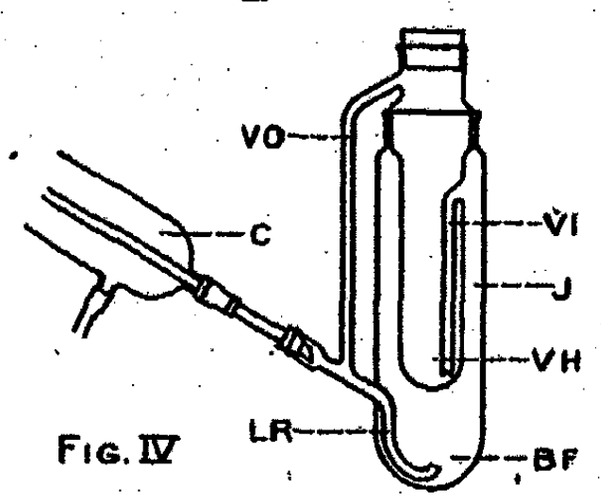


FIG. IV

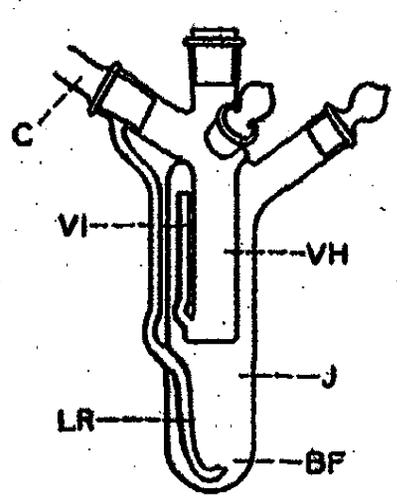


FIG. V

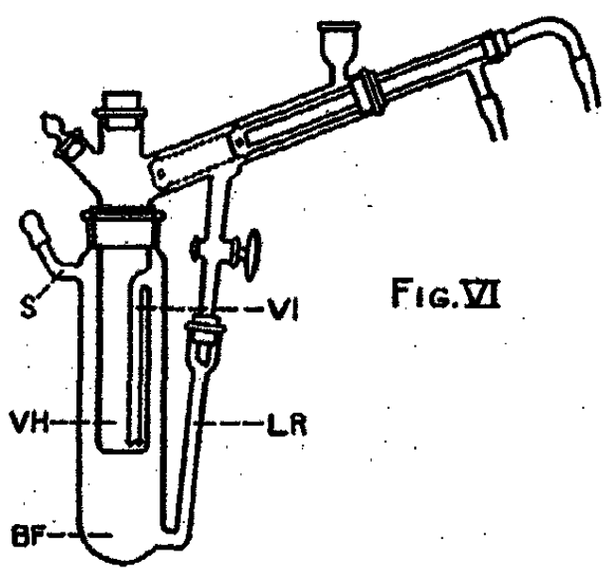


FIG. VI

inner tube; the vapor was led into the latter by means of a glass tube sealed to its wall (see Fig. 1).

To facilitate comparison and to avoid detailed description of the various forms which have been used, we have adopted the following uniform system of lettering in the accompanying figures:

BF is the boiling-flask containing the solvent; VD the vapor delivery tube, the tube through which the vapor passes from the boiling flask to the vapor heater; J the vapor jacket surrounding the vapor heater VH; VI the vapor inlet, the tube through which the vapor is passed into the vapor heater; VO is the vapor outlet; C the condenser; T the trap or valve; S the safety valve; LR the path of the liquid return. In some of the forms, not all of these parts are present.

The McCoy apparatus is seen to be a very compact and neat form but the use of cork to hold the inner tube in place causes trouble. To obviate this, the inner tube has either been sealed to the outer, or else a ground joint has been used. These improvements would have been satisfactory if it had been possible to replace the boiling flask easily, for the latter are too easily and too frequently broken. For this reason, Carveth[1] suggested the use of a jacketed vapor heater which might be attached to any type of boiling vessel. These are so compact, that of a number employed in this laboratory for various purposes none have been broken except by gross carelessness.

It is to be noted here that Smits[2] and also Meyer and Jaeger[3] have surrounded the inner tube by the boiling solvent and in other ways improved the Landsberger form. Ludlam[4] used a double-walled inner tube into which the vapor entered through an aperture near the top of the outer wall and a valve at the lower end of the inner wall. An objection to this form

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[1] Jour. Phys. Chem., 6, 324 (1902).
[2] Zeit. phys. Chem., 39, 408 (1901).
[3] Ber. chem. Ges., Berlin, 36, 1555 (1903).
[4] Jour. Chem. Soc., 81, 1193 (1902).

is that the solution in the inner tube may not be wholly prevented from flowing back into the boiling vessel.

The next stage of development of the method of vapor heating was that the solvent when finally condensed after its passage through the solution should be returned to the boiling flask; in other words, a continuous use of the same amount of solvent seemed necessary.

This idea was carried into effect by Riiber,[1] his design being shown in Fig. 2 which is self-explanatory. There is above the boiling solution but a small surface which may effect condensation; the main disadvantages are the cooling effect of the air on the long tube VD, and the several points of weakness of construction. If the condensation be prevented by proper insulation, and care be used, the apparatus is very serviceable.

The method of vapor heating now attracted the attention of Beckmann.[2] The form adopted, shown in Fig. 3, shows advantages over the forms previously described. The inner boiling tube may be filled by merely turning the condenser; after ebullition in VH is produced, the condenser is again turned and the liquid returns through T and LR. At this time one of us wrote :[3] "It is certain, however, that a vapor heater provided with a boiling vessel and trap will be far less fragile and just as serviceable as the new Beckmann type, whether the apparatus be used for molecular weight or for vapor composition work." An apparatus agreeing with this description had previously been made to carry out our work in dehydration by distillation, but the application to the determination of molecular weights had been unavoidably delayed.

The form of Lehner[4] shown in Fig. 4 has the advantage of being simpler and less expensive; like the Riiber, it offers very little surface for condensation and consequent dilution of the solution, but it also has no safety valve to prevent the sucking back of the liquid after ebullition has ceased; moreover it has

[1] Ber. chem. Ges., Berlin, 36, 1555 (1903).
[2] Zeit. phys. Chem., 40, 145 (1902).
[3] Carveth : Jour. Phys. Chem., 6, 146 (1902).
[4] Ber. chem. Ges., Berlin, 36, 1105 (1903).

the LR tube sealed into the boiling flask. In the opinion of the writers it is inadvisable to put into the hands of students any form which employs this method for returning the liquid since the boiling flask is so liable to break when being heated.

In 1903, Beckmann[1] described a later form; this is shown in Fig. 5. The most important changes are: (1) the former safety tube is abolished; (2) the returned liquid is delivered into the liquid below through a side tube which is sealed into the boiling flask; (3) the method of delivering the vapor into the vapor heater is changed. This new form is compact and should prove very serviceable. The principal objections to it are its cost, and the practical impossibility of replacing any part of it when broken. The experience of the writers is that the boiling flasks are broken very frequently, and the sealing in of a side tube is always a point of weakness. This same criticism must hold in regard to the form described and patented by Walther,[2] Fig. 6.

Since the Walker and Lumsden device of calibrating the inner tube enables the observer to determine by a simple volume reading the composition of the solution when the temperature reading is taken, the change of composition of the solution caused by condensation may be very readily followed. The amount of liquid actually condensed may, as a matter of fact, be surprisingly small, as is shown by the following results (Table I) which were obtained with an apparatus to be described later (Fig. 7). The amount of water put into the vapor heater was 10 cc; its temperature was 24°. The time count for the first reading was begun when the water in the boiling flask BF began to boil.

The boiling-point was thus reached in 3 minutes when the volume had increased 0.9 cc. In the next 30 minutes, the volume increased but 0.3 cc or 3 percent of the original volume. Since in the actual determinations, the temperature of the solvent in the vapor heater is at the beginning near its boiling-point, the condensation produced by heating the solvent

[1] Zeit. phys. Chem., 44, 161 (1903).

[2] Ber. chem. Ges., Berlin, 37, 78 (1904).

TABLE I

Time in minutes	Temperature range	Increase in volume in cc
2	24.0–99.0	0.7
1	99.0–99.4	0.2
3	99.4	0.1
5	99.4	0.05
7	99.4	0.05
15	99.4	0.10

to its boiling-point (as illustrated in the first two measurements of Table I) drops out of consideration. The slight increase in volume after the boiling-point has been reached proves that at 99.4° at least, the vapor heater is well protected from heat losses.

The points which we consider important in the construction of an apparatus for boiling-point determinations by the vapor heating method were: (1) the readings should be made quickly and accurately; (2) the parts liable to break should be easily replaceable; (3) a small amount of the solvent might be used if necessary; (4) the apparatus should be compact and easily manipulated.

The form devised is shown in Fig. 7, the dimensions being given in millimeters. The distinctive features of this form are a return condenser provided with a mercury trap, and a separate boiling vessel. The latter may be a round-bottomed flask of any size desired—150 to 200 cc is very satisfactory. For special cases the end of the vapor jacket may be ground to fit the neck of the boiling flask.

The condenser communicates with VH by the tube VO and with the boiling vessel by means of the tube LR. At T is a mercury trap (T) which, when open, allows the liquid from the condenser (C) to flow back into BF, and yet is of such a size that an appreciable amount of vapor cannot pass through it but must be forced into VH. When the trap is closed, the liquid will accumulate above the mercury and the vapor has no path other than through VI.

The narrow tube above T serves to hold a column of liquid which during the boiling is equal in weight to that forced down by the vapor in passing through VI; any increase in this column of liquid is returned through LR to BF by opening the trap. If the flame under BF is removed, the air cooling will cause

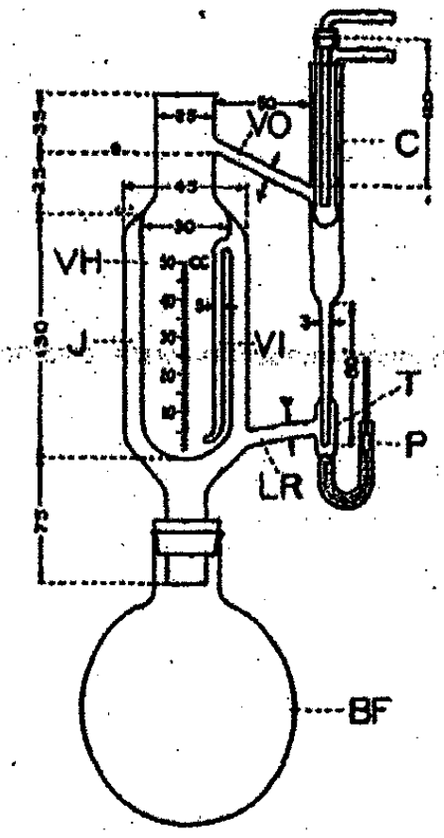


Fig. 7

a reduction of pressure in J; the column above T falls rapidly if the trap is open and there ensues an equalization of the internal and external pressures without any tendency to force the solution from VH into BF. This automatic adjustment appears to be of very decided advantage.

The dimensions have been selected after trying a number of variations. VH is 130 mm in length and 38 mm in internal diameter, the dimensions of the other parts being in proportion. It is important that VH should not be too short since with viscous liquids portions of the solution may be carried over.

The operation of finding a series of molecular weights by this apparatus is as follows: About 50 cc of the solvent are poured into BF and from 15 to 20 cc in VH. The boiling flask BF is then heated until the vapor is seen to be filling J. The

piston P is then lowered, causing the mercury to form a seal at T. The vapor is thus forced through the solution in VH, rapidly raising it to its boiling temperature. The condensed liquid falls back into the condenser arm and after it has risen to the end of the narrow tube, the trap T is opened sufficiently to allow the liquid to return, at such a rate as to keep the amount in the condenser arm constant. When the solvent shows constancy of boiling-point, the cork carrying the thermometer in VH is raised and the solid pellet dropped in. The next constant temperature is read, the flame removed, the thermometer taken out of the liquid, and the volume read. This gives the data for one determination. Another pellet may now be added, and the process repeated without renewing the solution or interrupting the heating except for the moment when the volume is being read. For water as solvent the liquid in VH should not exceed 35 cc; for low boiling liquids the volumes may exceed this.

Some of the determinations made with this apparatus are given in Table II. While the chemicals employed were C. P., the Beckmann thermometer employed had been checked only by the makers, Peters and Rost. The volume constants employed were obtained by dividing the constant ordinarily used by the density of the solution at its boiling-point. A few results of other observers are also given.

The results are very satisfactory except for benzoic acid and for sugar; even these came within the limit of error ordinarily allowed.

Because of the rapidity with which determinations can be made, the apparatus has been used with considerable success in lecture illustrations.

This paper contains:

1. A classified summary of the various forms of apparatus used in the determination of molecular weight by vapor heating methods.

2. The description of a new form suited for student use, the distinctive features of which as compared with the other

TABLE II

Solute	Weight Grams	Volume cc	Elevation	Mol. wt. found	Found by			Formula weight
					Walker and Lumsden	Landsberger	Beckmann	
Naphthalene	0.693	33.2	0.547°	125.1	139	144	144	128
"	0.693	40.7	0.430	129.0	141			
Alcohol as Solvent. (K = 1560)								
Urea	0.879	37.2	0.614	60.0	70	65	63	60
"	0.879	40.7	0.564	59.7	67			
					66			
Benzoic acid	0.617	27.7	0.317	109.6	122			122
" "	0.617	32.2	0.265	112.8				
Water as Solvent. (K = 5400)								
Sugar	0.692	18.5	0.059	342.0			356	342
	0.692	20.8	0.055	327.0			371	
	3.012	31.2	0.151	345				
	3.012	33.0	0.141	349				
	5.150	35.6	0.241	324				
	5.150	38.2	0.226	322				
Urea	0.411	18.9	0.180	65.2	63	62.6		60
	0.411	22.8	0.159	61.2	66	65.4		
	0.867	23.8	0.317	62.0				
	0.867	26.8	0.286	61.1				
	1.227	27.6	0.401	62.0				
KCl	0.769	19.1	0.517	42.5				74.5
	0.769	21.8	0.477	40.3				
	1.663	22.8	0.997	39.8				

types are (*a*) a separate boiling flask; (*b*) a return condenser provided with a mercury trap.

To Mr. Frank C. Robinson for his kind assistance in testing the earlier forms, we wish to express our hearty thanks.

Cornell University, April, 1905

THE RELATIONS BETWEEN STRUCTURE AND SMELL IN ORGANIC COMPOUNDS[1]

BY GERTRUD WOKER

The first essential for a smell is, of course, the volatility of a substance. Structural peculiarities and external conditions, which increase the volatility, increase the smell also as a rule. Although the substances with an odor vary very much in their chemical constitution, an examination shows that the large majority of them are unsaturated compounds and that the character of the odor varies with the degree of saturation. Very few substances, containing a triple bond, have a pleasant odor, though propargyl and diacetylene dicarboxylic ester do. In general, substances with a triple bond act so strongly on the nasal passages, and often on the bronchial tubes, that an unpleasantly stifling sensation is caused.

On the other hand, the presence of a double bond is often accompanied by a pleasant odor, as can be seen from the instances[2] in Table I.

TABLE I

Name	Smell	
Acetacetic ester	Fruity	Liquid
α-Methyl-β-oxyacrylic ester	Pleasant	"
Methyl malonate	Ethereal	"
Ethyl malonate	Aromatic	"
Ethyl oxalate	Spicy	"
Nitric ester	Pleasant	"
Nitroparaffine	"	Solid
Acetonylacetone	"	Liquid
Mesityl oxide	Like peppermint	"
Methyl heptenone	Ethereal	"
Tropylene	Like benzaldehyde	"
Dihydrobenzoic acid	Like cinnamon	Crystals volatile with steam.
Δ_2-Tetrahydrobenzoic acid	Like valerian	Liquid

[1] Translated from the author's German manuscript by W. D. Bancroft.

[2] The instances cited throughout this paper are taken from Krafft's "Lehrbuch der organischen Chemie."

TABLE I (*Continued*)

Name	Smell	
Cantharene	Like terpenes	Liquid
Dihydro-*p*-xylene	" "	"
l-Limonene	Like lemons	"
Inactive limonene	Pleasant	"
Pinene	Characteristic	"
d + *l*-Dihydrocarveol	Like terpinol	"
Terpinol	Pleasant	"
Tetrahydrocarvone	Like carvone	"
α-Furfurol	Aromatic	"
Furfuracrylic acid	Spicy	Needles
α-Thiophene aldehyde	Like benzaldehyde	Liquid
Geraniol	Pleasant	"
Linalool	"	"
Citronellal	"	"
Citral	Very pleasant	"
Pseudo-ionone	" "	"

Double bonds are also to be found in ionone, the artificial violet perfume; in irone from the violet roots; and in their derivatives, ionene and irene.

Compounds, containing a benzene ring, show an increase in the smell, especially when the phenyl radical is also connected with a double bond.

TABLE II

Name	Smell	
Phenol	Peculiar	Crystals
Naphthol	Like phenol	Leaflets
o-Chlorphenol	Unpleasant	Liquid
Thymol	Like thyme	Prisms
Creosol	Pleasantly aromatic	Liquid
Mesitylene	Aromatic	"
Cymol	Peculiar aromatic	"
Monochlor-benzene	Aromatic	"
Benzyl chloride	Stifling	"
Diphenyl-methane	Like oranges	Crystals
as-Diphenyl-ethane	Pleasant	Liquids
Tetra-hydronaphthalene	Like naphthalene	"
Nitrobenzene	Like benzaldehyde	"
Benzaldehyde	" "	"

TABLE II (*Continued*)

Name	Smell	
o-Tolulaldehyde	Like benzaldehyde	Liquids
m- "	" "	"
p- "	Peppery	"
Cumine aldehyde	Like cumine	"
Salicylic aldehyde	Peculiar	"
Vanilline	Like vanilla	Needles
Piperonal	Like heliotrope	Leaves
Cinnamic alcohol	Like hyacinth	Needles
α-Chlorstyrol	" "	Liquid
Eugenol	Like pinks, intense	"
Cumarine	Pleasant	Prisms

If the number of double bonds in a compound is increased beyond measure, the effect becomes similar to that of a triple bond. Instead of a plain increase in the intensity of the smell, there is a marked deterioration in the quality, accompanied by unpleasant irritating effects. Instances of this are given in Table III.

TABLE III

Name	Smell	
Acid anhydrides	Stifling	Liquid
Oxymethylene ketone	Penetrating	"
Dihydrobenzaldehyde	Stifling sweetish	"
Quinone	Like ozone	Volatile prisms
Toluquinone	Like quinone	Leaflets
p-Oxyloquinone	" "	Needles
Quinone chlorimide	" "	Volatile crystals
α-Naphthoquinone	" "	Plates

The quinones have four connected pairs of atoms each with a double bond. From the work of Witt, Liebermann, and v. Kostanecki it appears that the color of a substance and the presence of double bonds are connected in such a way that a substance is more intensely colored the more double bonds there are. Now it is remarkable that pairs of atoms with double bonds, 'chromophoric groups', also play an important

part in the case of odoriferous substances and that the increase of chromophoric groups in the molecule, i. e., the presence of 'complex chromophores', causes not only an increase in the color but often an increase in the smell. This surprising relation is especially evident in quinone where the double occurrence in series of the complex chromophore O:C.C:C is the cause of the color and the smell.

The effect of the double bond on the smell is best seen by a comparison of the saturated compounds with the corresponding unsaturated compounds (Table IV).

TABLE IV

C:C	C:C	C:C
Ethane, odorless	Ethylene, faint smell	Acetylene, strong unpleasant smell
Propane, odorless		Allylene, unpleasant smell.
Butane, odorless		Ethyl acetylene, strong smell.
		Dimethyl acetylene, peculiar smell
		Diacetylene, peculiar smell.
Hexane, faint ethereal smell	Diallyl, odor of horse radish	Dipropargyl, strong smell.
Propyl alcohol, ethereal smell	Allyl alcohol, pungent smell	
Propyl iodode, pleasant ethereal odor	Allyl iodode, garlic-like odor	
Propyl aldehyde, stifling odor	Acroleine, extremely irritating odor	Propargyl aldehyde worse than acroleine
Isopropyl alcohol, alcoholic smell	Acetone, characteristic smell	
Propionic acid, stifling smell	Acrylic acid, stifling acid smell	Propiolic acid, stifling acid smell

TABLE IV (*Continued*)

C.O	C:O
Butyl alcohol, peculiar smell	Butyl aldehyde, stifling odor
Isobutyl alcohol, peculiar smell	*n*-Butyric acid, most repulsive smell
Iso-amyl alcohol, peculiar smell	Isobutyric acid, disgusting repulsive smell
Ethyl alcohol, alcoholic odor	Isovalerianic acid, most disgusting smell
Methyl alcohol	Acetic acid, pungent smell
	Acetaldehyde, ethereal but stifling odor
	Formaldehyde, stifling smell
	Formic acid, pungent smell

C:C.C:O

Crotonaldehyde, odor stifling

C.N	C⋮N
Methylamine, ammoniacal smell	Prussic acid, most stifling odor
Ethylene diamine, ammoniacal smell	Cyanogen, intense odor
Dimethylamine, ammoniacal smell	Methyl carbylamine, frightful and disgusting odor.

From these data it appears that a substance has a more intense smell, the more double or triple bonds it has, or, in other words, the greater the internal tension. Two double bonds on the same carbon atom usually increase the smell of a substance more than a triple and a single bond. This can be seen from a comparison of the isocyanic esters with the normal esters (Table V).

TABLE V

Name	Smell
Normal cyanic esters	Ethereal smelling
Isocyanic esters	Unpleasant smelling, penetrating
Thiocyanic esters	Like garlic
Isothiocyanic esters	Stifling and irritating

If oxygen is replaced by sulphur, the smell becomes more marked and less pleasant (Table VI).

TABLE VI

Name	Smell
Methyl alcohol	Peculiar smell
Methyl mercaptane	Disgusting smell
Ethyl alcohol	Alcoholic smell
Ethyl mercaptane	Most disgusting smell
Phenol	Peculiar smell
Phenyl mercaptane	Intense smell of garlic
Benzyl alcohol	Aromatic smell
Benzyl mercaptane	Garlic-like smell
Acetone	Characteristic smell
Thio-acetone	Unbearable odor
Acetaldehyde	Peculiar ethereal and stifling
Thio-acetaldehyde	Very penetrating odor
Ethyl ether	Ethereal odor
Ethyl sulphide	Disgusting odor
Vinyl ether	Ethereal odor
Vinyl sulphide	Disgusting smell
Phenyl oxide	Odor like geraniums
Phenyl sulphide	Not unpleasant odor
Acetic acid	Pungent odor
Thio-acetic acid	Unpleasant, stifling odor
Carbon dioxide	Odorless
Carbonyl sulphide	Faint smell
Carbon bisulphide	Ethereal smell

Formaldehyde, thioformaldehyde, acetaldehyde and thioacetaldehyde all form odorless polymerization products having three times the molecular weight of the original substance. Since this condensation involves a disappearance of the double bonds, this is an additional proof of the great effect of the double bonds on the smell of a substance. Another instance of this is the polymerization of the volatile and stifling smelling cyanic acid, O:C:NH to the odorless cyanuric acid.

A compound can be unsaturated even when there is no double or triple bond, as for instance when an element does not show its maximum valence. Such compounds have the power of forming addition products just as much as substances containing multiple bonds. As a matter of fact it is hard to

draw a hard and fast line between an unsaturated atom and one that is connected with others by double bonds. It seems to me quite indifferent whether one speaks of a carbon atom with a double or triple bond or whether one says that the carbon atom is trivalent or bivalent. The two are different ways of expressing the same fact, that the substance is unsaturated at ordinary temperatures.[1]

Nitrogen is the most important of the elements which may have the same effect on a molecule as the presence of an atomic group with multiple bonds. Thus nitrogen is trivalent in the following compounds, all of which have characteristic smells: ammonia, methylamine, ethylamine, trimethylamine, ethoxyethylamine, *p*-diamidohexamethylene, dimethylene imine, trimethylene imine, pyrrolidine, α,α-dimethylpyrrolidine, piperidine, α-methylpiperidine, α,α-dimethylpiperidine. In a large number of nitrogenous substances we find the occurrence of a multiple bond in addition to trivalent nitrogen. This combination increases the intensity of the smell and often makes its quality worse, just as was the case when many multiple bonds were present in the molecule.

The following instances have already been referred to:

Prussic acid, its normal and iso derivatives.
Cyanic acid, its normal and iso derivatives.
Sulphocyanic acid, its normal and iso derivatives.
Cyanogen, chlorcyanogen, quinone chlorimide.

The following substances in Table VII come under the same head.

[1] If the temperature is raised, unsaturated compounds become saturated, i. e. the power of forming addition compounds decreases. It is a well known fact that acetylene is stable at high temperatures even in an atmosphere of hydrogen, in which it can be formed by the action of the arc. At high temperatures therefore it behaves like a saturated compound which cannot add on any other elements, and there is therefore no sense in writing the formula for acetylene under these conditions with a triple bond, since it has no longer any of the properties which are characteristic of the triple bond.

TABLE VII

Name	Smell
Cyanogen sulphide	Alkyl thionylamines
Acetamide	Diacetone amine
Allyl amine	δ-Propyl-δ-aminovaleraldehyde
Chlor-formamide	Trimethyl isoxazol
Alkyl nitrites	α-Pyrrolidon
α,α′-Methyl pyrrolidon	Pyrrol
Pyrroline	Pyrazol
Methyl glyoxaline	Osotriazol
Triazol	Pyridine
α-Vinyl pyridine	α-Chlorpyridine
β-Ethyl pyridine	α,α-Dimethyl pyridine
β,β-Dimethyl pyridine	Aldehydine
Nitrospiperidine	Nicotine
Tropidine	Ketazines
Pyrazine and pyrazine derivatives	Pyrimidine and pyrimidine derivatives
Hydronitric acid	

The combination of unsaturated nitrogen atoms with phenyl or naphthalene radicals causes an increase in the intensity of the smell similar to that caused by the union of atoms with a multiple bond to a phenyl radical. Instances of this are aniline, methylaniline, hydrazobenzene, benzonitrile, diphenylamine, phenylhydrazine, nitrobenzene α-naphthylamine, *ar*-tetrahydro-α-naphthylamine, *ar*-tetrahydro-β-naphthylamine, *ac*-tetrahydro-α-naphthylamine, *ac*-tetrahydro-β-naphthylamine.

We may also have the combination of trivalent nitrogen, phenyl radicals, and multiple bonds. It is to be expected that such compounds would have a very intense, usually unpleasant smell. The instances given in Table VIII show that this is true.

The phenyl and carboxyl derivatives of indol are not volatile and are therefore odorless.

What we have shown for nitrogen is probably also true for phosphorus. For the present, however, so few organic phosphorus compounds are available for comparison that we must confine our discussion to the phosphines. The disgust-

TABLE VIII

Name	Smell
Carbanyl	Unbearably stifling
Phenyl mustard oil	Stifling
Anthranil	Penetrating
α-Phenyl triazine	Peculiarly alkaloidal
α-Phenyl isoxazol	" "
Diazobenzene imide	Stupefying ammoniacal
Benzoyl azo-imide	Intense
Benzylidene ethylamine	Stifling
Isoquinoline	Peculiar
Quinoline	"
Methyl quinolines	Penetrating
Acridine	Pervasive
Phenanthridine	Suffocating
Indol	Very unpleasant
Skatole	Foecal-like
Ethylindoxyl	Indol-like
α-Methylindol	" "
α,β-Dimethylindol	" "

ing smell of hydrogen phosphide becomes more penetrating with successive replacements of hydrogen by alkyl, phenyl or toly. radicals, and is something fearful in the tertiary phosphines.

This increase in the smell through introduction of methyl groups appears to be a general phenomenon. Not only is the smell of an odoriferous substance increased but substances without smell can be converted in this way into compounds which do smell. Through successive replacements of hydrogen by methyl the smell of ammonia changes into that of pickled herring. Methyl quinone has a more penetrating odor than quinoline; skatole and dimethylindol smell stronger than indol; while the mercaptanes are much more unpleasant than hydrogen sulphide. By substitution we pass from the odorless propane to pentane which has an ethereal odor.

The phenomena with arsenic are similar to those with phosphorus. The most unpleasant smelling compounds are derivatives of trivalent arsenic. Arsenious hydride is more unpleasant than hydrogen phosphide and very much more unpleasant

than ammonia. The arsines are bad-smelling liquids. The cacodyl compounds are very much worse, thus illustrating the effect of the methyl groups. This is the place to refer to the onion-like smell of trimethyl antimonide and to the unpleasant odor of trimethyl bismuthide.

These few phosphorus, arsenic, antimony and bismuth compounds must be considered as unsaturated because the elements appear in their trivalent form. More important, however, than these are the derivatives of bivalent sulphur. A large number of these have already been cited in Table VI. A few more are given in Table IX.

TABLE IX

Name	Smell
Thiophene	Characteristic
Thienyl sulph-hydrate	Most unpleasant
Thiophene alcohol	Faintly aromatic
Thiophene aldehyde	Like benzaldehyde
Thiophthene	Tarry
Oxythionaphthene	Like phenol

It is to be noted that the invariable impurity of benzene, thiophene, is changed by the addition of an aldehyde group, just as benzene is, into a substance which smells like the oil of bitter almonds. This might be looked upon as a mere accidental coincidence were it not for the fact that the other derivatives of thiophene smell very like the corresponding benzene and naphthalene derivatives, as may be seen from Table X.

TABLE X

Name	Smell
Naphthalene	Peculiarly tarry
Thiophthene	Tarry
α-Naphthol	Like phenol
Oxythionaphthene	" "
Benzyl alcohol	Aromatic
α-Thiophene alcohol	Faintly aromatic
Phenyl mercaptane	Most unpleasant
Thienyl sulph-hydrate	" "

It appears almost as though the sulphur atom were capable of replacing two CH groups without causing any essential change in the smell or other properties of a compound. This similarity of properties would be of course the reason for the difficulty in separating benzene from thiophene, and toluene from methyl thiophene. All the compounds in which sulphur has its lowest valency are characterized by a more or less intense and unpleasant smell. If one compares with these the compounds in which sulphur is either quadrivalent or hexavalent, it appears that these latter are either odorless or have a relatively pleasant smell as in the case of the alkyl esters of sulphurous and sulphuric acids. In the esters of sulphurous acid there is one double bond while there are two in the esters of sulphuric acid. A natural consequence of this is that the smell is more intense in the odoriferous derivatives of sulphuric acid than in the corresponding derivatives of sulphurous acid. Sulphur dioxide, however, has a very irritating effect; but it has two double bonds.

It has already been pointed out in this paper that the sulphur compounds usually have more of a smell and a worse smell than the corresponding oxygen compounds. This may be explained on the basis that substances with bivalent sulphur are unsaturated even when there are no double bonds and that the bivalent sulphur increases the effect of double bonds, when present, just as trivalent nitrogen increases the effect of multiple bonds.

Lately, the view has been gaining ground that oxygen is quadrivalent in some compounds. In that case one could ascribe the odor of alcohols and ethers to the presence of an unsaturated oxygen atom. That substances containing oxygen have a less marked smell than those containing sulphur would then be explained on the ground that bivalent sulphur is much more unsaturated than bivalent oxygen, as shown by the lesser readiness of the latter to assume and hold a higher valence.

Even if one were satisfied with this explanation for the odor of alcohols and ethers there still remain many substances

which are undoubtedly saturated and which yet smell. A striking case of this is hexachlorethane which smells like camphor and which crystallizes in plates that are volatile in the air. The following substances also have a camphor smell: camphor, trimethyl carbinol, acetone chloroform, dimethyl-allyl carbinol and higher alcohols of this series, durol, borneol, methyl tertiary butyl carbinol, ethylidene malonic acid, silicon tetra-ethyl, and silico-heptyl alcohol. While these substances, which smell like camphor, belong to all sorts of different classes, they all have one peculiarity in common, at least one carbon atom in which the hydrogen has been completely replaced by other groups. In every case at least two and usually three of the substituting groups are identical. The methyl group appears most often as a substituting group and chlorine is fairly well represented, while in one case there are two carboxyl groups and a double bond.

The presence of the double bond appears to be unimportant. The character of the fourth substituting group is of little importance except when it acts strongly against the other three. The effect of a negative carboxyl group, for instance, weakens the effect of three positive methyl groups.

Essential for the existence of a smell like camphor is the complete substitution of all the hydrogen attached to a carbon atom and the substituting groups should be as much alike as possible. In this way the intramolecular repelling forces become especially great and the increase of the internal pressure causes a maximum volatility.

A strong smell is characteristic of all substances in which a carbon atom is overloaded with identical groups, either positive or negative. This is brought out in Table XI.

TABLE XI

Name	Smell
Chloroform	Strongly ethereal
Bromoform	" "
Iodoform	Characteristic
Trichlornitromethane	Stifling
Chloral	Pervasive
Chloral hydrate	Peculiar
Dichlor-acetone	Pungent
Thiocarbonyl chloride	Suffocating
Perchlor methyl mercaptane	Unpleasant
Ethylidene chloride	Ethereal

In harmony with this is the fact that normal alkyl derivatives of a substance almost always have a fainter odor than the iso derivatives while these have a fainter odor than the corresponding tertiary compounds (Table XII).

TABLE XII

Name	Smell
n-Valerianic acid	Repulsive
Isovalerianic acid	More repulsive
Trimethyl acetic acid	Stifling acid
n-Butyl alcohol	Peculiar
Secondary butyl alcohol	Intense
Isobutyl alcohol	Unpleasant
Tertiary butyl alcohol	Like camphor

Artificial musk, one of the most strong smelling substances, has a carbon atom united to three methyl groups. A carbon atom overloaded with methyl groups is to be found in the hydrocyclic compounds (Table I); in the most closely related aromatic substances (Table II) such as cymol, thymol, carvacrol and others; and in the related substances with open rings such as citral, etc. Most of the perfumes come under the mentioned heading of substances which combine great volatility with the property of affecting the nasal passages pleasantly. The volatility is brought about by the overloading of the carbon atom with methyl groups while the scent is due to the presence of double bonds.

The closing of the ring is only of minor importance both in regard to smell and to other properties. The pleasant odor of the terpenes and their oxygen derivatives remains after the ring is broken. As an instance we may take the often-cited citral and compare it with pulegone In other types the slight effect of closing the ring can be shown (Table XIII).

TABLE XIII

Name	Smell
Tetra methyl carboxylic acid	Like fatty acids
n-Valerianic acid	Repulsive, sour
Pentamethylene carboxylic acid	Sour
n-Caproic acid	"
Hexahydrophenol	Like fusel oil
n-Amyl or capryl alcohol	" " "
Diethylamine	Ammoniacal
Pyrrolidine	"
Ethyl acetamide	Like acetamide
α-Pyrrolidon	" "

Cases may, however, arise in which the closing of the ring has an effect. This will happen when the closing of the ring is accompanied by a marked increase in the internal tension. Thus trimethylene has a faint smell while propane is odorless. Erythrit ether has a pleasant odor while erythrit has practically no smell. Glycidic acid has an irritating smell which does not occur in glyceric acid. The same contrast is to be found between the sharp smelling propylene oxide and propylene glycol.[1] In di- and tri-methylene imines an accentuation of the ammoniacal smell can be noticed, as compared with dimethyl- and methyl-ethylamine. Dimethyl ketone and its lower homologues have an aromatic smell which changes to a strong odor of peppermint in di-tetra methylene ketone.

According to Baeyer's tension theory it is to be expected that the closing of the saturated five-membered ring would have the least effect on the properties and especially on the smell because the system closes without perceptible change in tension. So far as is known, the facts are in accord with this view.

The closing of the six-membered ring and still more of the seven-membered ring causes, however, an increase in tension which shows itself in an increase in the odor. Ethyl propyl ketone and dipropyl ketone smell like acetone. On changing into keto-hexamethylene and suberone respectively, a strong smell like peppermint is developed precisely analogous to what can be observed in the closing of the ring with ditetramethylene ketone. The sign of the tension change in ditetramethylene ketone is, however, the opposite of that for keto-hexamethylene and suberone. In addition, it is to be noted that the closing of the ring always has an immense effect upon the odor if the multiple bonds of a system are affected thereby, as in the case of paraldehyde or cyanuric acid.

A few anomalous cases must now be discussed. It has been shown that multiple bonds usually cause the smell and that the intensity of the smell increases with increasing accumulation of multiple bonds. Quite apart from unsaturated side chains, benzene derivatives possess three double bonds while the di- and tetra-hydro addition products have two and one respectively. We should therefore expect the genuine benzene derivatives to have a more noticeable odor than the hydrogen addition products. This is by no means the case, as may be seen from Table XIV.

TABLE XIV

Name	Smell
Benzene	Peculiar
Dihydrobenzene	Garlic-like
Tetrahydrobenzene	" "
Benzoic acid	Peculiar
Dihydrobenzoic acid	Like cinnamon
Δ_2-Tetrahydrobenzoic acid	Like valerian

Also carvomenthol, with its odor of orange blossoms, and other hydrocyclic compounds have a stronger smell than the corresponding aromatic compounds, such as carvacrol for instance.

This peculiar behavior agrees also with other observations wherein benzene behaves in many respects as though it were more saturated than the really unsaturated di- and tetra-addition products (Thiele).

As a matter of fact these and other observations have caused some people to draw the conclusion that there are no double bonds in benzene. This conclusion is unquestionably right if one looks upon a 'double bond' as something unchangeable. There are, however, no conclusive reasons for assuming the unchangeability of the state which one calls the double or the triple bond. The facts favor the opposite view that we have to deal with something changeable, which depends on temperature, pressure and the nature of the substituting groups. The degree of saturation and consequently the number of 'bonds' varies with the conditions. There are cases known in which the constitution of the substances shows that they unquestionably contain double bonds and yet a suitable substitution will cause these substances to lose their power of adding on substances. This power to form addition products can also disappear with rising temperature, as has already been pointed out. Such substances behave exactly as though they were saturated compounds and that is probably what they are.

Something similar is obviously true for benzene, whose three double bonds are modified by cross connections and so bring about a very peculiar state which is half way between that of a saturated and an unsaturated compound.

Another anomaly is to be found in compounds of the uric acid group. The molecule of uric acid is composed entirely of groups which increase the odor; namely, three carbonyl groups, one ethylene group, and four unsaturated or trivalent nitrogen atoms. In spite of this, uric acid is entirely odorless and, in spite of four chromophoric groups, it has no color. It is quite possible that these remarkable phenomena are connected with the fact that a decrease in the refraction and dispersion takes place when the carbonyl group is united directly

to the amino group (*Zeitschrift für physikalische Chemie*). The decrease in the refraction and the dispersion constants would be significant of an approach to a saturated state. The cause of the decrease in the constants and especially of the absence of smell is perhaps to be found in the fact that the carbonyl group has a markedly negative character while the amino or imino group is strongly positive. The attraction between these two opposing complexes may decrease the volatility for this is on the other hand increased by the presence of two like, and therefore mutually repelling, groups. This molecular attraction between positive and negative parts of a molecule is possibly also the reason why metallic salts of volatile acids are not volatile and are therefore odorless.

Mention must also be made of the odoriferous saturated compounds which show a normal structure and apparently no overloading of a carbon atom with identical groups. Among such substances are pentane, hexane and heptane which are all very volatile and which all have a noticeable ethereal odor. Other instances are the methyl halogen compounds, CH_3Cl, etc. If one writes the formulas for these compounds a little differently, pentane becomes a diethyl methane, hexane an ethyl propyl methane, and heptane a di-propyl methane. The odor of pentane and heptane would be explicable on the basis of two identical groups attached to the same carbon atom. The odor of hexane is much fainter, as was to be expected from the substituting groups being similar but not identical.

The smell of the saturated secondary alcohols and ethers can be explained in the same way if one does not care to fall back on the unsaturated oxygen atom.

The volatile monohalogen derivatives of the saturated hydrocarbons, methyl fluoride, methyl chloride, methyl iodide, and also the primary alcohols are characterized by the fact that the hydrogen combined with the halogen in the halide acid or with the hydroxyl in water has been completely replaced by a methyl or a homologous alkyl group. These compounds are therefore to be classed with those in which a

complete substitution of hydrogen by alkyl groups has occurred. The only difference is that there is only one replaceable hydrogen atom in a halide acid. The behavior of these halogen compounds could also be explained as due to an unsaturated halogen, since the halogen may have a valence of seven.

The most important results of this paper may be summed up as follows:

1. An odoriferous substance must be volatile.

2. An odoriferous substance may be a saturated or an unsaturated compound. The first case is rare and the smell is then perceptible only when the substance is extremely volatile.

3. The volatility is increased especially by overloading a carbon atom with identical groups. Substances, in which all the hydrogen of at least one carbon atom has been replaced, often have an odor like camphor when at least two of the substituting groups are identical. Such a system has the maximum volatility. Under these circumstances it is indifferent whether the compound is saturated or unsaturated, though three of the substituting groups must be the same if the compound is saturated. The nature of the fourth is important only when it works against the other three.

4. The combinations of groups which increase the volatility and smell of saturated compounds act similarly in the case of unsaturated compounds.

5. Everything else being the same, the odor of a compound increases in intensity as the degree of saturation decreases.

5*a*. Substances with a triple bond usually have a more marked odor than substances with a double bond.

5*b*. The presence of several double or triple bonds increases the smell.

5*c*. Presence of an unsaturated atom may also be the cause of a substance having a smell.

5*d*. The combination of unsaturated atoms and of mul-

tiple bonds increases the smell just as does the presence of several multiple bonds.

5*e*. The greatest increase in odor is obtained when the same substance has multiple bonds, unsaturated atoms, plain or hydrogenized phenyl or naphthalene radicals, and carbon atoms all of whose hydrogens have been replaced.

6. It may happen that a combination of groups may nullify the smell even when each group by itself would increase it. This occurs with the uric acid compounds where electropositive imido groups are attached to electronegative carbonyl groups. The mutual attraction of these complexes causes a pressure exerted inwards while a pressure exerted outwards is essential to volatility. This latter tension can obviously be obtained through the repelling action of similar groups.

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ELECTROLYTIC CORROSION OF THE BRONZES

BY B. E. CURRY

It is well known that many of our useful metals and alloys are materially affected by corroding agents. Iron rusts in the air, steam pipes corrode and leak, the brass commonly known as Muntz metal dissolves in sea water. Some of the metals form protecting films that prevent further action. Beyond the formation of a thin gray film tin does not rust; the same is true of aluminum and some other metals. At the present time the corrosion of alloys has been studied but little. It is known that certain brasses dissolve in the same ratio as the copper and zinc present, while other brasses dissolve differently.

Many of the other properties of the useful alloys have been studied in detail, and it is the purpose of this research to study the corroding effects of some of the more common reagents on the copper-tin series of alloys. The equilibrium diagram has been determined by Shepherd and Blough, and the tensile strength[1] tests have already been published.

The work of Shepherd and Blough has shown that five solid phases occur in bronzes annealed between 200° and 400°. From 100 percent to 87 percent copper we have a series of solid solutions known as the α crystals. From 87 percent to 74.5 percent the alloys consist of mixtures of α and δ crystals in varying proportions. From 74.5 percent to 67 percent we have the δ crystals, a series of solid solutions. These are the crystals which Heycock and Neville believed to be the compound Cu_4Sn. Between 67 percent and 61.3 percent we have mixtures of δ crystals with the compound Cu_8Sn, this latter occurring pure at 61.3 percent copper. Cu_8Sn and the ε crystals coexist from 61.3 percent to 41 percent. From 41 percent to 40 percent we have a new series of solid solutions, the ε crystals. Pure tin and ε crystals coexist between 40 percent and 0 percent copper.

[1] Shepherd and Upton : Jour. Phys. Chem., 9, 441 (1905).

The test-pieces were made from very pure electrolytic copper and 99.99 percent tin, the alloys were melted in Acheson graphite crucibles and cast in cylindrical graphite moulds. They were 8.5 centimeters long and 0.8 centimeter in diameter. The copper was always melted first in the presence of powdered graphite and illuminating gas. After complete fusion of the copper, the tin was added, the melt stirred thoroughly, and then poured. Any bronze may be obtained by this method. The test-piece should be removed from the mould and quenched as soon as sufficiently cold to permit handling. After quenching, the ingots were annealed. The annealing process was carried on in a nickel wire resistance furnace. The process is at an end when equilibrium is reached, as shown by the microscopic examination. After a little experience it is easy to tell fairly accurately, even without the microscope, how long a given alloy should be annealed. All bronzes annealed above 500° must be quenched rapidly in order to prevent the formation of the phases stable at lower temperatures.

After annealing, the test pieces were cleaned and all traces of oxide removed by means of a file or carborundum paper. Each piece was then numbered and weighed.

In order to make the results more comparable and to save time, the electrolytic tests were run in series. An apparatus was so arranged that five tests could be carried on simultaneously, the same current passing through each test-piece as anode. Platinum wire was used for cathodes.

Each test-piece was mounted on the shaft piece of a small Ajax motor by means of a large brass connector. the motors were used only as bearings, and each was driven separately by a belt from a shaft which was connected to a large motor. This arrangement permitted a uniform rate of motion for each test-piece. When once adjusted, the test-pieces were rotated rapidly and steadily. In this way each solution was kept well stirred and uniform throughout. Without effective stirring, uniform results cannot be hoped for.

Test-pieces of the following percentage composition of copper were made: 95, 90, 85, 80, 75, 70, 65, 60, 55, 50, 45, 40,

35, 25, 15, 5. This series is sufficiently complete for our purpose. Hereafter, all percentages are referred to copper unless otherwise stated.

The effect of electrolytic corrosion was examined in solutions of sodium sulphate, sodium nitrate, sodium acetate, alkaline sodium tartrate, acid ammonium oxalate, sodium chloride, and copper sulphate.

Tests on chemical corrosions were made by bubbling air through solutions of sodium persulphate, alkaline sodium persulphate, sodium carbonate, and sodium chloride.

At the end of each test, the bronze was removed from the solution and carefully cleaned with a rubber-tipped stirring rod. All wash water was added to the original solution. In most cases a very satisfactory cleaning may be secured by a few minutes of patient work. After being cleaned and dried each piece was heated in a stream of hydrogen until all oxides were reduced. The amount of corrosion may then be determined by reweighing the test-piece, and subtracting this weight from the original weight.

All electrolytic tests were carried on in special thick-walled 250 cc beakers. About 200 cc solution were employed for each test. After the test-piece was removed and cleaned, the solution was acidified with nitric acid. The copper was precipitated electrolytically and weighed. If the copper deposit was not bright, or was found to contain tin, it was reprecipitated and reweighed. The tin was determined by difference. Knowing the percentage of copper in the corrosion products and in the original alloy, it was known whether the alloy was becoming tin-rich or copper-rich as a result of the corrosion.

In most tests 7 percent solutions were used. These were found to be more satisfactory than the more concentrated solutions where the salt crystallizes and creeps over the edge of the beaker.

Neutral solutions were chosen because they could be kept almost uniform, and at the same time the introduction of sol-

uble copper and tin salts was prevented. In the neutral solutions these salts were precipitated as hydroxides the instant they were formed. In neutral solutions the tendency of the dissolved copper to reprecipitate on the test-piece is obviated. It is difficult to prevent the reprecipitation of copper from acid solutions. The same is true for soluble copper salts in alkaline solutions.

Ordinarily the tests were made at room temperature which was subject only to slight variation.

In all tests, a surface of about 13.8 cm^2 was exposed to the solution. In the electrolytic tests a current of about 25 milliamperes was used. This gives a current density of 0.18 amp/dm^2. The time for each run was about eight hours.

Electrolytic Corrosion in Suphate Solutions

A 7 percent solution of sodium sulphate was employed for this series of tests. The results obtained in the sulphate solutions are given in Table I which, as all subsequent tables, is

TABLE I

7 Percent Sodium Sulphate Solution

Percentage of copper in test-piece	Corrosion in grams	Grams copper corroded	Percentage of copper corroded
95	0.3787	0.3638	96.07
90	0.3617	0.3411	94.3
85	0.1289	0.1245	97.3
80	0.0850	0.0812	95.6
75	0.0416	0.0400	96.1
70	0.0070	0.0060	
65	0.0061	0.0036	
60	0.0041	0.0030	
55	0.0037	0.0030	
50	0.0052	0.0040	
45	0.0049	0.0039	
40	0.0015	0.0009	
35	0.0410	0.0126	30.1
25	0.1579	0.0213	3.3
15	0.2629	0.0224	8.5
5	0.3707	0.0121	3.2

arranged as follows: The first column gives the composition of the test-piece in percentage of copper; the second the amount

of corrosion; the third the amount of copper in the corrosion product; the fourth the percentage of copper in the corrosion product. In this series of tests the α and δ bronzes were annealed at 400°; the Cu_3Sn and ϵ were annealed at 217°.

There is no apparent difference in the way in which the 95 percent and 90 percent bronzes dissolve. In a given time with the same current, both solutions contain about the same bulk of oxides. The solubility of the 85 percent, 80 percent and 75 percent bronzes is much less, and decreases very rapidly in the order named. There is a very marked tendency for these to become passive. The 70 percent bronze is practically insoluble. The bronzes between 70 percent and 40 percent do not dissolve in sulphate solutions. With less than 40 percent copper content all of the bronzes corrode in sulphate solutions. The 35 percent bronzes dissolve only slightly (the dissolved portion is almost pure tin), and the amount of corrosion increases as the copper content decreases. All these changes can be detected in a rough way by the appearance of the electrolyte as the action continues.

The corroding action does not change the appearance of the 95 percent bronze except for a slight tendency to become tin-rich on the surface. The 90 percent bronze becomes tin-rich as the action continues; this tendency is slight, but more marked than in the 95 percent bronze.

The 85 percent, 80 percent, 75 percent, 70 percent, bronzes become decidedly tin-rich. The surfaces of the 85 percent, 80 percent and 75 percent have the appearance of metallic tin. The 65 percent, 60 percent, 55 percent, 50 percent, 45 percent, 40 percent bronzes dissolve so slightly that there is no apparent change. All bronzes with less than 40 percent copper content become copper-rich on the surface. There is not a marked tendency for the copper-rich, or α bronzes, to become passive. The α crystals dissolve almost without change. The 95 percent and 90 percent bronzes are composed of pure α crystals. The 85 percent, 80 percent and 75 percent bronzes are composed of a mixture of the two phases α and δ. These latter form a protecting film on the surface which tends

to make the bronze passive. Because of the presence of the soluble α phase, the film is porous, and the corrosion continues but at much reduced rate. The 74 percent bronze is composed of homogeneous δ crystals. The protecting film formed on this bronze is only slightly porous and very effective. The film on the δ bronzes is tin-rich and easily detected.

The bronzes between 74 percent and 40 percent copper content form a very thin invisible film on the surface. Its presence can be detected when the bronze is heated in a hydrogen atmosphere. There is always a slight loss in weight when so treated.

All bronzes with less than 40 percent copper content have the phases ε and pure tin in equilibrium. The ε phase becomes passive, and the tin dissolves. The solubility increases as the ε phase decreases in amount. The 35 percent bronze dissolves slightly, while the 5 percent bronze dissolves very readily. There is a tendency for these bronzes to disintegrate as the corrosion continues. Tin is dissolved from around the ε crystals, and these finally fall into the solution but do not dissolve.

The first results obtained in the sulphate solutions were puzzling for a time. The amount of copper in the corrosion product was often greater than the anode loss. The methods of analysis were checked and found to be correct. The anodes were then reduced in hydrogen, and in the process lost considerable weight. This explained the difficulty, and at the same time showed that the protecting film was some form of oxide. At first sight the film has the appearance of metallic tin.

In Figure I is shown the efficiency curve for the series of tests. This curve is not absolute, but represents the facts in hand. The data were obtained in part by extrapolation, and are not given here.

The horizontal line A B represents the concentration of copper and tin with the pure components at A and B respectively. The current efficiency is represented vertically from the line

A B with 100 percent efficiency at C and D for the pure copper and tin, copper being considered as bivalent, and tin as quadrivalent. All other efficiency curves are presented in this way except that copper is considered as univalent, and tin as bivalent in chloride solutions. To bring out

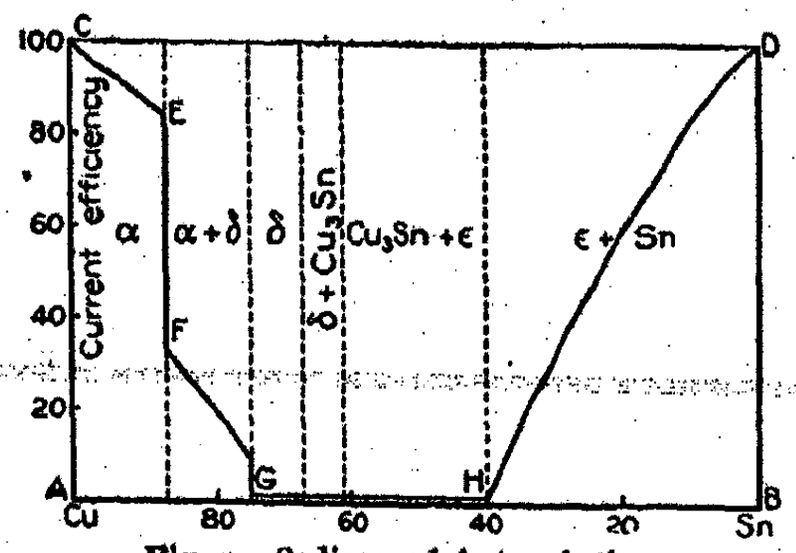


Fig. 1. Sodium sulphate solution

the relation between corrosion and composition more clearly, the fields for all the phases except pure ε are indicated by means of dotted lines.

The efficiency curve consists of four branches. The branch C E represents the efficiency for the α bronzes; F G for the $\alpha+\delta$ bronzes; G H for the δ, δ + Cu_3Sn and Cu_3Sn + ε bronzes; and H D for the ε + Sn bronzes. These are very distinct branches, and conform very closely to the equilibrium diagram. The efficiency for δ, Cu_3 Sn, and ε bronzes is almost zero, and the curve is almost flat over this range. The two soluble phases are α and tin. When either of these is in equilibrium with an insoluble phase the efficiency drops very rapidly.

From the nature of the corrosion of the ε and Sn bronzes it was evident that almost no ε was dissolved. Accordingly, a short run was made on these. Care was taken to remove any undissolved ε crystals from the solution before proceeding with the analysis. The results are recorded in Table II.

Practically, the ε does not dissolve at all, and the corrosion product is pure tin. The high copper content found in the corrosion product for the ε and Sn bronzes recorded in Table I

is due to the fact that the entire corrosion product was dissolved before analyzing for the copper. Even there the copper content is much lower than in the test-piece.

TABLE II

7 Percent Sodium Sulphate Solution

Percentage of copper in test-piece	Corrosion in grams	Grams copper corroded	Percentage of copper corroded
35	0.0390	0.0007	1.7
25	0.0985	0.0004	0.4
15	0.1967	0.0007	0.4
5	0.1058	0.0020	1.9

Electrolytic Corrosion in Nitrate Solutions

For this series of tests, a 7 percent solution of sodium nitrate was used.

The α and δ bronzes were annealed at 400°, the Cu_3Sn and ϵ at 217°.

The results are recorded in Table III.

TABLE III

7 Percent Sodium Nitrate Solution

Percentage of copper in test-piece	Corrosion in grams	Grams copper corroded	Percentage of copper corroded
95	0.2528	0.2452	97.0
90	0.2593	0.2386	92.0
85	0.2513	0.2471	98.2
80	0.2555	0.2386	93.0
75	0.1142	0.1000	87.5
70	0.0507	0.0415	81.8
65	0.0049	0.0038	
60	0.0087	0.0061	
55	0.0037	0.0024	
50	0.0040	0.0032	
45	0.0027	0.0032	
40	0.0045	0.0043	
35	0.0491	0.0077	15.7
25	1.7904	0.3783	21.7
15	1.2990	0.1824	14.0
5	1.0752	0.0433	4.3

The behavior of the bronzes is similar to that in the sulphate solutions. The α bronzes dissolve readily, and tend to become tin-rich on the surface, but only very slightly. The $\alpha + \delta$, and δ bronzes become decidedly tin-rich on the surface. The protecting film has little effect on the bronzes poor in δ. This is most likely due to its porosity. The 75 percent bronze which is almost pure δ forms a protecting film which is fairly stable. The δ,$\delta + Cu_3Sn$, $Cu_3Sn + \varepsilon$, and ε bronzes are insoluble. These form a very thin protecting film which does not break down in nitrate solutions. The bronzes with less than 40 percent copper content corrode in nitrate solutions. The amount of corrosion is slight where the bronze is

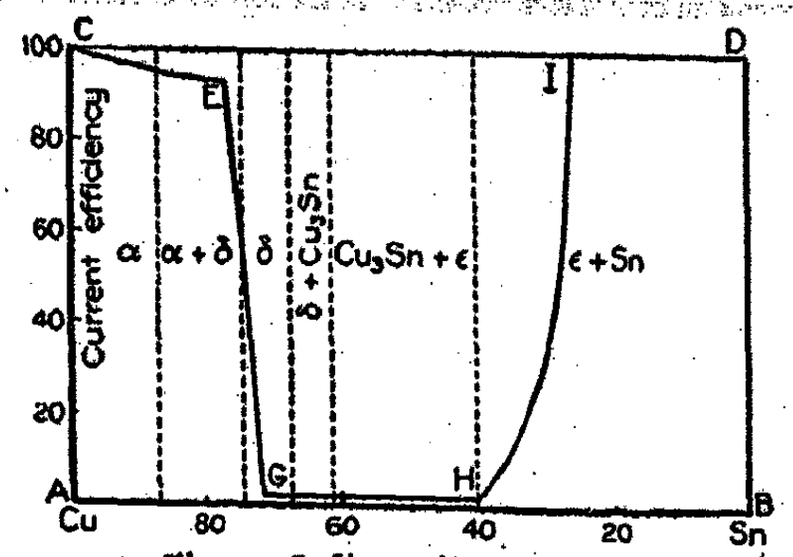


Fig. 2. Sodium nitrate solution

nearly pure ε but increases as the bronzes approach pure tin. This is due to the fact that the ε crystals are not soluble as compared to pure tin. The tin soon disappears, and forms a bronze rich in the ε phase, and the solubility must then decrease.

Ordinarily we would expect tin to dissolve as stannic nitrate in nitrate solutions. This is found to be contrary to fact. When a tin anode is run in series with a copper voltameter the amount of corrosion is practically 2.5 times that found in the voltameter. We would expect the tin anode to lose practically the same weight as does the copper, or in fact, a little less.

Figure 2 shows the efficiency curve for this series of tests. The branch C E represents the efficiency for the α and $\alpha + \delta$

bronzes. This curve is continuous and regular until almost the pure δ bronze is reached. At a composition near 75 percent the efficiency drops very rapidly and continues very low through the δ bronzes. The sudden drop is seen in the part of the curve E G. Over the range from 70 percent to 40 percent copper content the branch G H is flat. The δ + Cu_3Sn, Cu_3Sn + ε, and ε bronzes do not dissolve. With less than 40 percent, copper, the corrosion goes on at an abnormal rate as already noted. The 35 percent bronze dissolves with a low efficiency. With still less copper content the branch H I rises very abruptly, and extends to a point representing about 250 percent for pure tin.[1]

Table IV gives the results obtained for a short run in nitrate solutions. Care was taken here to remove the ε crystals from the solution before analyzing for copper. The analyses show that the ε crystals are not dissolved in the nitrate solutions, but are dislodged when the cementing material, or pure tin is dissolved away.

TABLE IV

7 Percent Sodium Nitrate Solution

Percentage of copper in test-piece	Corrosion in grams	Grams copper corroded	Percentage of copper corroded
35	0.0565	0.0008	1.4
25	0.2355	0.0046	1.9
15	0.1463	0.0025	1.6
5	0.2198	0.0013	0.6

Some bronzes having the following compositions, 85 percent, 80 percent, 75 percent, 70 percent, 65 percent were annealed at 625° and quenched in water. The phases present in this series are α, β, γ and Cu_3Sn. On quenching, the 70 percent bronze broke into many pieces, and its corrosion properties could not be determined. A short piece of the 65 percent bronze was finally obtained from this temperature. These

[1] It is probable that tin is bivalent when anode in nitrate solution and that the extra 25 percent loss is due to disintegration.

bronzes were treated in the same manner as the bronzes in the previous test. The results are given in Table V.

TABLE V

7 Percent Sodium Nitrate Solution

Percentage of copper in test-piece	Corrosion in grams	Grams copper corroded	Percentage of copper corroded
85	0.3150	0.2950	93.6
80	0.3170	0.2908	91.7
75	0.0581	0.0503	86.5
65	0.0235	0.0220	85.1

The behavior of the β and γ bronzes is not unlike that of δ. The efficiency for the $\alpha+\beta$ bronzes is practically the same as for $\alpha+\delta$. β dissolves slightly in the beginning but becomes passive very quickly. The 65 percent bronze which represents $\gamma + Cu_3Sn$ does not dissolve. The $\beta+\gamma$ bronzes are very brittle, and can scarcely be quenched to prevent breaking. All these bronzes become tin-rich on the surface.

The efficiency curve for these bronzes is shown in Figure 3 by the curve C E G H. The branch C E coincides with the

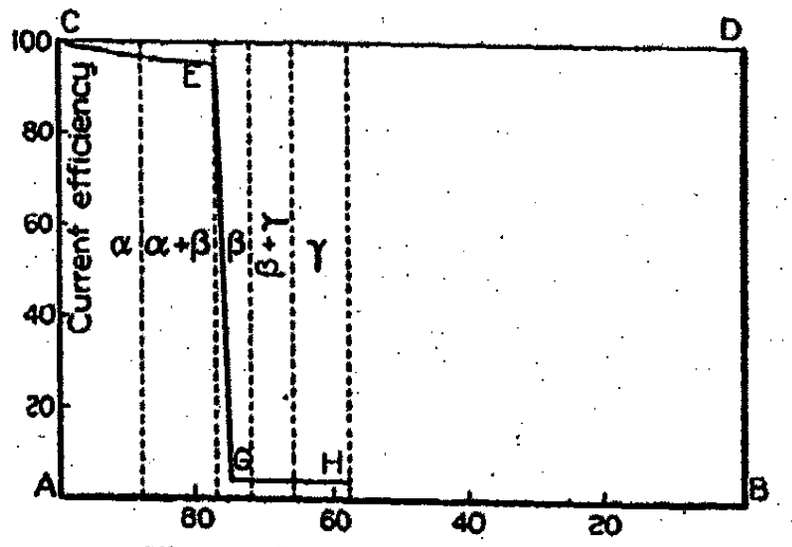


Fig. 3. Sodium nitrate solution.

corresponding branch of the curve for the $\alpha+\delta$ bronzes. The branch corresponding to β, $\beta+\gamma$, γ, $\gamma+Cu_3Sn$ is flat.

Since the β and γ bronzes behave in the same way as the δ bronzes in nitrate solutions, they would undoubtedly behave in the same way toward other corroding agents. For

this reason and also because of the difficulty of obtaining suitable test-pieces of $\beta + \gamma$ bronzes, no further study was made of these.

Electrolytic Corrosion in Acetate Solutions

For this series of tests a 7 percent solution of sodium acetate was employed. The α and δ bronzes were annealed at 400° and all others at 217°. The results are given in Table VI.

TABLE VI

7 Percent Sodium Acetate Solution

Percentage of copper in test-piece	Corrosion in grams	Grams copper corroded	Percentage of copper corroded
95	0.0843	0.0826	98.0
90	0.0271	0.0268	98.2
85	0.0073	0.0068	93.1
80	0.0032	0.0034	
75	0.0019	0.0024	
70	0.0023	0.0020	
65	0.0022		
60	0.0013	0.0002	
55	0.0015	0.0016	
50	0.000	0.0005	
45	0.0006		
35	0.0735	0.0020	2.7
25	0.2478	0.0059	2.4
15	0.2251	0.0046	2.4
5	0.3233	0.0017	0.5

Only two phases dissolved in the acetate solutions. The α phase dissolves tin-rich on the surface. An increasing amount of tin in the α bronzes decreases the amount of corrosion rapidly. The δ bronze does not dissolve at all, and its presence prevents the corrosion of the α phase. The 85 percent bronze corrodes only very slightly. The Cu_3Sn and ε bronzes do not corrode at all. With less than 40 percent copper content the tin dissolves, and the ε crystals are left behind. The 35 percent bronze corrodes only slightly, the free tin content being very low. The amount of corrosion increases as the ε content decreases. The 15 percent bronze corrodes three times as fast as the 35 percent bronze.

The efficiency curve for this series is given in Figure 4 The branch E F represents the efficiency for the α bronze. The branch F G, which is almost flat for its entire length, represents the efficiency for the $\alpha + \delta$, δ, $\delta + Cu_3Sn$, $Cu_3Sn + \varepsilon$, and ε bronzes. These do not dissolve at all. The branch G D represents the efficiency for the ε + Sn bronzes.

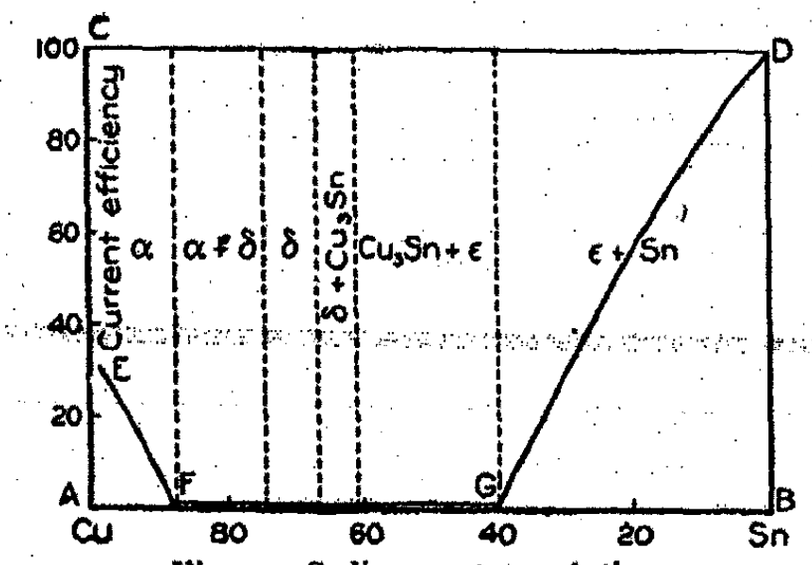


Fig. 4. Sodium acetate solution

Corrosion in Carbonate Solutions

A series of tests were made in a 7 percent solution of sodium carbonate. The results are given in Table VII.

TABLE VII

7 Percent Sodium Carbonate Solution

Percentage of copper in test-piece	Corrosion in grams
95	0.0021
90	0.0029
85	0.0030
80	0.0031
75	0.0040
70	0.0039
65	
60	
55	0.0039
50	
45	0.0050
35	0.0028
25	0.0086
15	
5	0.0019

The bronzes do not corrode in carbonate solutions. The loss in weight at the anode was only very slight at the end of a 7 hour run. It is quite evident that the green carbonate that forms on the surface of bronze exposed to the air must first dissolve as some other salt which is afterwards changed to a carbonate.

Electrolytic Corrosion in Alkaline Tartrate Solutions

For this series, a solution of 7 percent sodium tartrate and 5 percent caustic soda was used. The results are given in Table VIII.

TABLE VIII

7 Percent Sodium Tartrate Solution + 5 Percent Caustic Soda

Percentage of copper in test-piece	Corrosion in grams	Grams copper corroded	Percentage of copper corroded
95	0.2770	0.2610	94.3
90	0.2628	0.2373	90.3
85	0.2551	0.2206	86.5
80	0.2474	0.1976	80.3
75	0.2353	0.1767	75.1
70	0.2300	0.1598	69.5
65	0.1380	0.0877	64.3
60	0.1200	0.0727	60.2
55	0.0767	0.0427	55.6
50	0.0550	0.0284	51.6
45	0.0600	0.0241	46.3
35	0.3501	0.0755	21.6
25	0.4809	0.0321	6.8
15	0.5607	0.0296	5.2
5	0.5383	0.0073	1.4

All bronzes corrode in alkaline tartrate solutions. The α and δ bronzes dissolve without change. The $\alpha + \delta$ bronzes undergo a slight change. The α phase dissolves first, and leaves a surface richer in δ crystals. After this shift takes place, the solution continues without further change, and the corrosion product has the same composition as the bronze. This shift is slight, and is not easily detected by analysis when the amount of corrosion is great. The $\alpha + \delta$ bronzes become tin-rich on the surface. The appearance of the α and δ bronzes

is little changed. The appearance of the δ + Cu_3Sn, Cu_3Sn + ϵ, and ϵ bronzes is not changed by corrosion. The corrosion product has the same composition as the bronze. The ϵ + Sn bronzes become copper-rich on the surface. The free tin dissolves first, and the ϵ crystals are left behind. However, the ϵ crystals are broken down to a certain extent, and a considerable amount of copper is found in solution, but this is always much less than the copper content of the bronze.

The bronzes do not form a protecting film in the alkaline tartrate solutions, and the corroded bronzes do not lose weight when heated in hydrogen.

The efficiency curve is shown in Figure 5. This curve consists of three branches. The branch C E represents the

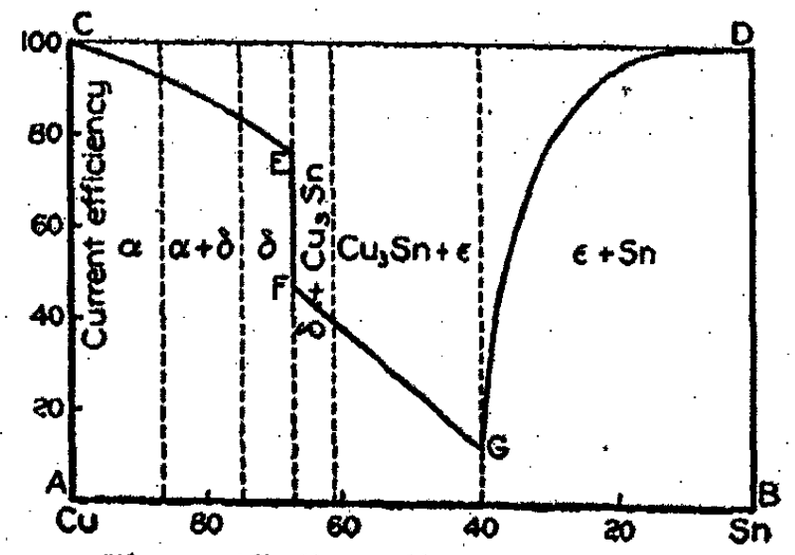


Fig. 5. Alkaline sodium tartrate solution

efficiency for the α, α + δ and δ bronzes. The branch F G represents the efficiency for the δ + Cu_3Sn, and Cu_3Sn + ϵ bronzes. The Cu_3Sn is less soluble than the δ, and the efficiency drops for these bronzes. The ϵ is less soluble than the Cu_3Sn, and the efficiency drops to a minimum at a 40 percent copper content, or for pure ϵ. The branch G D represents the efficiency for the ϵ and Sn bronzes.

Electrolytic Corrosion in Acid Oxalate Solutions

For this series of tests, a solution containing 3 percent ammonium oxalate and 3 percent oxalic acid was used. The results are given in Table IX.

All bronzes corrode in acid oxalate solutions. In general, the behavior is the same as in the alkaline tartrate solutions. The anodes remain perfectly clean and bright throughout the

TABLE IX

3 Percent Ammonium Oxalate Solution + 3 Percent Oxalic Acid

Percentage of copper in test-piece	Corrosion in grams	Gram copper corroded	Percentage of copper corroded
90	0.2310	0.2086	90.1
85	0.2390	0.2037	85.2
80	0.2432	0.1948	80.1
75	0.2416	0.1819	75.3
70	0.2531	0.1772	70.1
60	0.1820	0.1102	60.5
50	0.1263	0.0644	51.0
40	0.0659	0.0255	38.6
15	0.4349	0.0044	1.0

run, and do not lose weight when heated in hydrogen. There is but slight tendency for the α and δ bronzes to go tin-rich. The efficiency curve is shown in Figure 6. The curve is not

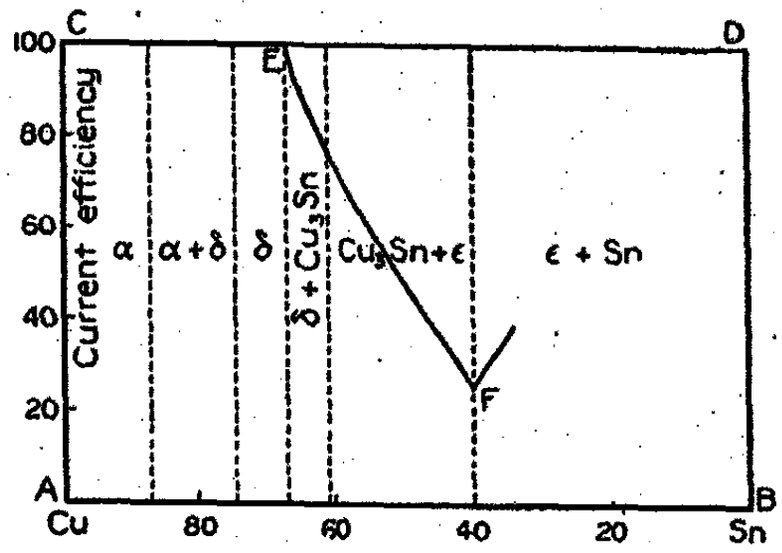


Fig. 6. Acidified ammonium oxalate solution

completed for the ε + Sn bronzes, but for these the tin and some ε dissolve. The α, and $\alpha + \delta$ bronzes give practically 100 percent efficiency in this solution. The curve has a minimum at 40 percent copper content, or for the ε bronze.

Electrolytic Corrosion in Chloride Solution

The chloride tests were run in a 7 percent solution of sodium chloride. The results are given in Table X.

In chloride solutions the α bronzes dissolve without change while the α and δ bronzes become tin-rich on the surface. The α phase dissolves first, and leaves a surface rich in δ. After this shift takes place the bronze continues to dissolve without further change. The δ, $\delta + Cu_3Sn$, $Cu_3Sn + \varepsilon$ bronzes undergo very little change if any. The ε + Sn bronzes go copper-rich on the surface because the tin dissolves and leaves the ε phase.

TABLE X

7 Percent Sodium Chloride Solution

Percentage of copper in test piece	Corrosion in grams	Gram copper corroded	Percentage of copper corroded
95	0.3486	0.3318	94.9
90	0.3478	0.3135	90.1
85	0.3216	0.2775	86.3
80	0.3282	0.2694	82.0
75	0.2793	0.2106	75.4
70	0.2416	0.1701	70.4
65	0.2462	0.1611	65.4
60	0.2537	0.1538	60.3
55	0.2598	0.1402	54.0
50	0.2736	0.1363	49.8
45	0.4021	0.1802	44.8
35	0.3693	0.0525	14.2
25	0.3051	0.0584	19.1
15	0.4425	0.0448	10.1
5	0.4237	0.0169	3.8

The chloride solutions are the most difficult of any to deal with. The copper and tin dissolve as cuprous and stannous chloride; basic salts form, and the solution becomes alkaline. Unless the alkalinity is kept down by the addition of acid, a thick adherent scale forms on the test-piece. In an alkaline solution, the tin is removed from this scale, and it becomes rich in copper. When cleaning the test-piece, before reduction in hydrogen, all chlorides should be removed, otherwise both copper and tin are distilled off.

The bronzes do not become passive in chloride solutions. An 80 percent bronze was made anode in a sulphate solution

until well coated with the protecting film. The piece was then transferred to a chloride solution where it began to dissolve immediately.

The efficiency curve for this series is given in Figure 7. The curve is continuous, has no marked irregularities, and approximates the theroretical values.

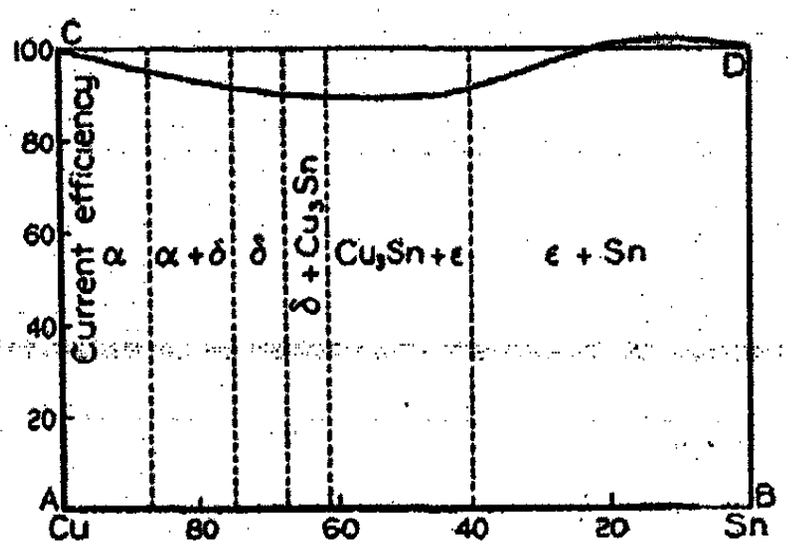


Fig. 7. Sodium chloride solution.

In Table XI is recorded the results of a run in sodium chloride in which the solution became alkaline and remained

TABLE XI

7 Percent Sodium Chloride Solution

Percentage of copper in test-piece	Corrosion in grams	Gram copper corroded	Percentage of copper corroded
75	0.0968	0.0655	67.6
70	0.1077	0.0609	56.4
65	0.1103	0.0642	58.2
60	0.1014	0.0468	45
55	0.1182	0.0561	47.4
50	0.1123	0.0372	33.1
40	0.1809	0.0402	22.2
35	0.1380	0.0207	15.0
25	0.1598	0.0171	10.7
15	0.1395	0.0020	1.4
5	0.1541	0.0020	1.3

so. The adherent crust of oxides was not removed. At the end of the run, the test-pieces were removed and washed, but not scraped in any way. When dried, each piece was reduced

in hydrogen and weighed. It is at once evident from the analysis that the scale was copper-rich. The tin has been removed from the mass of precipitated hydroxides, and the copper left behind. In the reduction of the unremoved scale some tin and a little copper were lost by distillation. But aside from this, the analyses show the effects of the alkaline solution. The scale is a corrosion product, and may be removed. When this is done, the new surface is not different from the original and the corrosion product and the test-piece have the same composition.

In order to compare the effects of chemical corrosion with those of electrolytic corrosion, some measurements were made in sodium persulphate solutions without bubbling air in, and in sodium chloride solutions through which a continuous stream of air passed. It was expected that the sodium persulphate solutions would give results comparable with those obtained by the electrolysis of sodium sulphate solution. It was also hoped that the corrosion by air in presence of sodium chloride would be similar in nature to the electrolytic corrosion in sodium chloride solutions. The analogy is not absolute. The chemical corrosion would be identical with the electrolytic corrosion if we had bubbled chlorine into the solution. As no one cares how the bronzes corrode in presence of chlorine this experiment was not tried. On the other hand, oxygen, as an oxidizing agent, stands between chlorine and bromine, and the apparent differences are due to the possibility of passivity in presence of oxygen. Since metals do not become passive in chloride solutions, it was thought probable that the electrolysis of chloride solutions would give a fairly accurate measure of the corrosion by air in chloride solutions.

Chemical Corrosion in Sodium Persulphate Solutions

For this series of tests, a 20 percent solution of sodium persulphate was used. The test-pieces were allowed to stand in the solutions for sixteen days. The results are given in Table XII.

The α bronzes dissolve without change in persulphate solutions. The $\alpha + \delta$ bronzes become tin-rich on the surface. The α phase dissolves first, and leaves the tin-rich δ phase behind. The δ, $\delta + Cu_3Sn$, $Cu_3Sn + \varepsilon$, and ε bronzes do not corrode rapidly in persulphate solutions. These become passive, and little further solution takes place. The ε + Sn bronze corrode, and go copper-rich on the surface. The pure tin dissolves first and the ε crystals are left.

TABLE XII
20 Percent Sodium Persulphate Solution

Percentage of copper in test-piece	Corrosion in grams	Grams copper corroded	Percentage of copper corroded
95	4.1613	3.9490	94.9
90	0.6269	0.5645	90.2
80	0.2748	0.2617	95.2
65	0.0664	0.0620	93.4
50	0.0085	0.0060	70.5
25	0.1256	0.0098	7.8

In persulphate solutions, the soluble phases are α and tin. The 95 percent test-piece was dug out in deep holes, the surface remained very bright and free from adherent oxides. The appearance of the 90 percent piece was less changed. The surface was less pitted, and the amount of corrosion much less. The 85 percent and 65 percent pieces were tin-rich on the surface. The 65 percent and 50 percent pieces were coated with an oxide and were only slightly corroded. The 25 percent piece was pitted, and the slime contained undissolved ε crystals.

Chemical Corrosion in Alkaline Persulphate Solutions

For this series, a 20 percent solution of sodium persulphate was made strongly alkaline with caustic soda. The test-pieces were allowed to stand in the solutions for sixteen days. The data are given in Table XIII.

In alkaline persulphate solutions, the α bronzes dissolve without change. The α and δ bronzes go tin-rich on the surface. The δ, $\delta + Cu_3Sn$, $Cu_3Sn + \varepsilon$ bronzes are only slightly corroded. The ε + Sn bronzes become copper-rich. The corrosion product contains ε crystals intact. The bronzes examined behave in the same way towards both the neutral and alkaline persulphate solutions. The behavior here is not different from that in the electrolytic tests with sodium sulphate solutions.

TABLE XIII

20 Percent Sodium Persulphate Solution + Excess Caustic Soda

Percentage of copper in test-piece	Corrosion in grams	Grams copper corroded	Percentage of copper corroded
95	2.4075	2.3038	95.2
90	1.5424	1.3924	90.3
80	0.0829	0.0746	90.0
65	0.0063	0.0047	74.6
25	1.6478	0.2558	15.5

Chemical Corrosion in Sodium Chloride Solution

In this series of tests a 7 percent solution of sodium chloride was used and air was bubbled through the solution continuously. In this way oxygen was supplied and at the same time the solution was kept well stirred. The following bronzes were examined: 95 percent, 85 percent, 70 percent, 65 percent, 60 percent, 50 percent, and 25 percent. The results are given in Table XIV.

TABLE XIV

7 Percent Sodium Chloride Solution

Percentage of copper in test-piece	Corrosion in grams	Gram copper corroded	Percentage of copper corroded
95	0.0954	0.0916	96.0
85	0.0534	0.0480	88.2
70	0.0563	0.0390	69.4
65	0.0450	0.0296	65.8
60	0.0400	0.0240	60.2
50	0.0430	0.0129	51.0
25	0.0360	0.0022	6.0

The α bronzes dissolve without change and fairly rapidly. The $\alpha + \delta$ bronzes dissolve less rapidly and become tin-rich on the surface. The α crystals dissolve first and leave the surface rich in δ crystals. The δ, $\delta + Cu_3Sn$, $Cu_3Sn + \varepsilon$, and ε bronzes corrode very slowly and undergo very little change if any during the process. The ε + Sn bronzes become copper-rich, the Sn dissolving first.

In this experiment the 95 percent, 85 percent and 25 percent pieces were subjected to the action of the salt solution and oxygen for five weeks. The others were allowed to run nine weeks. It is at once evident that the action goes on very slowly, especially where the δ, Cu_3Sn, and ε bronzes are involved. While the α bronzes corrode very appreciably a single determination necessitates much time.

The observations made on chemical corrosion conform very closely to those made in the electrolytic way. For this reason and also because of the great amount of time involved a more thorough study of the chemical effects was not made. However, we are of the opinion that a more extensive study would only prove more conclusively that the same general results may be obtained in much less time by the electrolytic method. By shortening the time factor from two months to one day the process may be observed more closely and the introduction of undesirable factors prevented.

Electrolytic Corrosion in Miscellaneous Solutions

To determine the effect, if any, of an ammonium salt, test-pieces of 85 percent and 75 percent copper content were run in series in 7 percent solutions of ammonium sulphate. The 85 percent piece lost 0.2351 gram in weight, and the 75 percent lost 0.0130 gram. The corrosion product from the 85 percent bronze was 98 percent copper, and from the 75 percent bronze 90 percent copper. The electrolytic corrosion with ammonium sulphate is therefore practically the same as with sodium sulphate. The next experiment was made to find out whether the presence of a copper salt in solution would check the dissolving of copper from the anode.

The 75 percent and 65 percent bronzes were run in series in a 7 percent solution of copper sulphate. The 75 percent piece lost 0.0174 gram, and the 65 percent piece lost 0.0055 gram. Both went decidedly tin-rich on the surface. The corrosion product was not analyzed. The electrolytic corrosion in a solution containing copper sulphate is practically the same for the copper-rich bronzes as the electrolytic corrosion in sodium sulphate solution.

To show the effect of temperature, a 60 percent bronze was made anode in a sodium sulphate solution for two hours in a temperature of 80° C with a current of 0.025 ampere; the anode loss was 0.025 gram. This difference of temperature is not sufficient to change the effectiveness of the protecting film.

Analysis of the Protecting Film

Both tin and copper dissolve quantitatively when made anode in salt solutions. The bronzes do not dissolve quantitatively. The film which forms on these bronzes causes the efficiency to drop. This fi'm is apparently tin-rich, and when the corrosion has proceeded far enough, the film may be removed in quantities. A few grams of this film were obtained for analyses. After reduction to the metallic condition, the copper content was found to be near 20 percent, but this was subject to variation. As some or perhaps all of this copper might have been retained mechanically, a different method was tried.

Another portion of the film was placed in a platinum crucible, and a solution of sodium sulphate added. The crucible was made anode, and the solution electrolyzed. The gray powder broke down, and very nearly pure stannic oxide remained undissolved. This insoluble residue was analyzed, and found to contain less than 1 percent copper. If this film were a compound, there is no evident reason why it should have broken down under these conditions.

This evidence points to the conclusion that the film is stannic oxide with more or less occluded copper. The film used

for these tests was obtained from an 80 percent bronze. Attempts to form a compound from the oxides of copper and tin in a fused bath were without success. The film is formed electrolytically only in solutions in which stannic oxide would be stable. It is not known why certain alloys should give it and others not, and it is also not known why there is a formation of a film rather than of a powder.

In connection with these corrosion experiments we found that the pure block-tin water pipes in the laboratory were badly corroded. The gray surface film which forms under ordinary conditions had broken down and the pipes were coated with a white powder similar to stannic oxide in appearance. Portions of this corrosion product were removed and examined for the presence of the common laboratory acids. Sulphates, chlorides, and nitrates were found to be present in quantities. In other laboratories where acids were used to a less extent the tin pipes were less corroded. In laboratories where almost no acids were used the pipes were normal in appearance and showed almost no evidence of corrosion.

From these observations it is evident that the protecting film found on pure tin surfaces breaks down in the presence of the stronger acids and that corrosion then takes place more rapidly. In air or in the presence of oxygen and CO_2 this film is stable and almost no corrosion takes place. The electrolytic observations on pure tin are very similar to those obtained chemically. Pure tin corrodes very readily in sulphate, chloride and nitrate solutions when treated electrolytically but almost no corrosion takes place in the carbonate solution.

The corrosion results show the impracticability of the solution method for proving the existence of metallic compounds. When a two-phase alloy is dissolved it must go into solution unchanged or one phase will dissolve faster than the other.

In the case of the $\alpha + \delta$ alloys it has been shown that the α phase dissolves first and that the δ phase is left behind. When the residue is analyzed it is found to be richer in tin than the original alloy. Its composition is something near 75 percent copper and this points to the existence of the compound

Cu_4Sn. However, the range of concentration over which δ crystallizes pure varies from 67 percent to 74 percent copper.

Almost pure tin dissolves from the ϵ and Sn bronzes and the residue consists of almost pure ϵ crystals which show about 40 percent copper when analyzed. This indicates the compound CuSn. It is now certain from the microscopical examination of the annealed alloys that ϵ crystallizes pure over a range of two percent.

Heycock and Neville[1] worked on these particular cases but their very careful work failed to establish the exact equilibrium relations. Their evidence pointed to the existence of Cu_4Sn and of CuSn, neither of which exist. Solid solutions may form a very insoluble phase which may easily be mistaken for a compound. Unless the solubility observations are supplemented by other evidence the conclusions may be in error.

Summary

In this research the following results have been obtained:

The electrolytic corrosion effects have been determined in some of the more common salt solutions.

The electrolytic results have been checked by straight chemical tests and the two have been found to agree closely.

The α bronzes corrode more rapidly than any others. In all solutions and by all methods these undergo but little change in the process.

The $\alpha + \delta$ and $\alpha + \beta$ bronzes corrode tin-rich on the surface.

The β, δ, $\beta + \gamma$, $\delta + Cu_3Sn$, $Cu_3Sn + \epsilon$ and ϵ bronzes undergo little change and tend to become passive.

The ϵ + Sn bronzes corrode copper-rich on the surface and tend to disintegrate as the tin dissolves.

The cause for certain of the bronzes becoming passive has been found to be the formation of a film of stannic oxide.

This film has been obtained in quantities and its composition determined.

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[1] Phil. Trans., 202A, 1 (1904).

The *e* bronze withstands corroding action better than any other.

No bronze becomes passive in chloride solutions.

The efficiency curves have been presented for a number of solutions.

A change in the rate of corrosion occurs only at the appearance or disappearance of a phase in the equilibrium diagram.

Quantitative relations have been established throughout the work.

This work has been done under the direction of Prof. Bancroft to whom the author is much indebted for kindly advice and criticism.

The expenses of this research have been covered by a grant from the Carnegie Institution of Washington, D. C.

Cornell University, May, 1906.

ELECTROLYTIC PRECIPITATION OF LEAD FROM ACETATE SOLUTIONS

BY RALPH C. SNOWDON

Under ordinary conditions the electrolysis of lead acetate solutions gives large feathery crystals of lead which fall from the cathode to the bottom of the cell. Even if an excess of acetic acid be added, there is no marked change in the size of the crystals or in the quality of the deposit. This solution seemed therefore an admirable one on which to try the methods which had previously proved successful with silver nitrate[1]. It had been shown that rapid motion of the electrolyte, produced either by rotating the cathode or by stirring, tends to make the deposit smoother and to reduce the size of the crystals. It was also shown that the size of the crystals of deposited metal decreases with increasing current density until conditions are reached where the speed of the rotating cathode is not sufficient to burnish the rapidly precipitated masses of metal. Following out the "chemistry" conception of electrolytic precipitation I used a solution of lead acetate and acetic acid, normal with respect to each. Knowing from much previous experience that a satisfactory deposit of lead could not be obtained without stirring, I tried a rotating cathode made of a copper tube having a wetted surface of 10 cm^2. This was speeded to about 2500 revolutions per minute. A lead anode was used. At a low current density, 0.5 amp/dm^2, the metal deposited from this solution in a crystalline and adherent form, almost entirely without the "flaky" appearance which is so noticeable with a stationary cathode. At higher current densities, however, the deposit kept growing worse and worse, falling off in leafy crystals. This was probably because the speed of rotation of the cathode was not high enough for the speed of precipitation, the two always being interdependent to a greater or lesser extent.

[1] Snowdon : Jour. Phys. Chem., 9, 392 (1905).

Since it was not feasible to increase the speed of rotation of the cathode, I next tried the addition of gelatine to the solution. One gram of gelatine per liter was added; the temperature was kept at 30°; the cathode density was 1.5 amp/dm²; and the other conditions were as in the preceding runs. A matte deposit of lead was obtained, very adherent and entirely satisfactory in every way. It is not claimed that a lead acetate solution would be a desirable one to use in precipitating lead. There are other solutions, notably the fluosilicate, which give an adherent deposit of lead over a much wider range of conditions. The object of the paper was to show that it is quite possible to get a good plating deposit of lead even from an acetate solution and that the favorable conditions are the same for lead as for other metals.

This work was suggested by Prof. Bancroft and carried out under his direction.

Cornell University.

FERROMANGANESE ANODES IN CAUSTIC SODA SOLUTIONS

BY G. R. WHITE

Lorenz[1] has shown that potassium permanganate is formed when ferromanganese is made anode in a dilute caustic potash solution. On repeating this experiment with varying conditions, the green manganate was often obtained. It looked as though this was a case in which the nature of the product varied markedly with varying conditions. In the fifth American edition of Richter's "Inorganic Chemistry," page 391, it is stated that the red permanganate solution changes to the green manganate on addition of an alkaline hydroxide. Assuming this to be true, the favorable conditions for the manganate would be a concentrated alkali and a high temperature. Since the valency of manganese is higher in the permanganates than in the manganates, it might be thought that a high anode density would favor the formation of the more highly oxidized substance, the permanganate. This last assumption is of doubtful accuracy, but the experiments apparently confirmed all the predictions. Cast ingots of ferromanganese, with a surface of approximately 10 cm^2, were used with platinum wire cathodes. With a 2 percent solution of sodium hydroxide, made from "pure sticks," and a current of 1.25 amperes, permanganate was formed when the electrolysis was carried on at ordinary temperatures. With a 10 percent solution and a current of 0.25 ampere, manganate was obtained. At 90°, manganate was formed under all conditions of concentration and current density. While this was apparently very satisfactory, there were some facts which did not fit in. Under all circumstances, there was a layer of red solution immediately in contact with the anode. This made it appear as though the ferromanganese always dissolved as permanganate, in which case the formation of manganate

[1] Zeit. anorg. Chem., 12, 393 (1896).

would be a secondary reaction having nothing to do with the electrolytic phenomena. When a current of 1.25 amperes was run through a 10 percent caustic soda solution for an hour and a half, the green color change gradually to the pink permanganate. On the other hand, it was noticed that an alkaline solution of permanganate becomes green if allowed to stand over night in an open beaker. These apparent contradictions disappear if the statement in Richter's is wrong, and if the following quotation from Roscoe and Schorlemmer[1] is right:

"The permanganates are converted into manganates with evolution of oxygen when their solution in concentrated caustic potash is boiled:

$$2KOH + KMnO_4 = 2K_2MnO_4 + O + H_2O.$$

"The same change occurs when reducing agents, such as alcohol and sodium thiosulphate, are added to the solution, only so much, of course, being added as suffices for the reduction of the permanganate to manganate. The red alkaline solution turns blue and afterwards green on exposure to the air, this being caused by the reducing action of the *organic matter*[2] contained in the atmosphere."

No experiments have been made to determine how concentrated the caustic potash must be in order to cause the permanganate to break down when the solution is boiled; but the reaction does not take place with 50 percent caustic soda. One thing, however, is certain, and that is that organic matter or other reducing substances are necessary for the reduction of permanganate to manganate in alkaline solutions at temperatures up to 100°.

The change on standing over night is to be explained as follows: The solution contains only a relatively small amount of permanganate, and is strongly alkaline. Under these conditions, organic dust particles falling into the open beaker, bring about the reduction to the manganate:

$$2KMnO_4 + 2KOH = 2K_2MnO_4 + H_2O + [O]$$

[1] Vol. II, Part II, p. 19 (Edition 1886).

[2] Italics are mine.

The fact that a green color is produced in all cases on diffusion of the permanganate into the electrolyte indicates that the electrolyte contains organic matter, and this view is confirmed by the fact that the green color persists longer in the concentrated than in the dilute and disappears sooner when the current is high, or in other words, when the amount of permanganate being formed is relatively large.

Assuming then that organic matter is necessary for the reduction of the permanganate to manganate, an effort was made to overcome this contamination as much as possible. In the first place, up to this time the beakers in which the electrolysis was carried on were covered with wooden electrode holders. Inasmuch as hydrogen was given off at the cathode and oxygen at the anode, it was thought that these gases might tend to carry the alkali mechanically up to the cover, the sodium hydroxide would then act on the cover, and, sooner or later, drop back into the electrolyte, laden with organic material. Furthermore, the base might attack and weaken the wooden cover so that particles of wood might drop into the solution. Any organic matter thus introduced would most certainly aid in the formation of the manganate. For this reason, glass covers were substituted for the wooden, in the subsequent experimental work. Again, it was found that with commercial sodium hydroxide, the green color persisted much longer than with a better grade of the alkali—the commercial, doubtless, being more contaminated with organic matter because of careless handling.

Therefore, in order to rid the electrolyte of any organic matter, it was decided to add enough permanganate to make the solution pink. With this precaution, it would be safe to assume that the electrolyte was free from any organic material. Runs were made, using the same current strengths and the same concentrations as before. The 2 percent solution, with 0.25 and with 1.25 amperes, started pink and remained pink after running for two hours, in each case. Likewise, the 10 percent solution, with the same current strengths as above,

remained pink after a similar period of time. For this reason, it seems very probable that the production of anything but permanganate at ordinary temperatures is due entirely to the presence of some reducing agent in the solution.

The question now comes up, "How may we explain the fact that the permanganate, on standing over night, becomes green?" In answering the question, it must be remembered that, after all the organic or other reducing agents have been removed, it requires only a very small quantity of permanganate to give the solution a pink color. Furthermore, some time is required before the reaction.

$$2K_2MnO_4 + 2KOH \xrightarrow{\text{containing organic or other reducing agents}} 2K_2MnO_4 + 2H_2O + [O]$$

comes to equilibrium. No study has been made of the exact speed of this reaction, but from cursory observations, it is noticed that at first the reduction goes on rapidly and completely, but gradually slows down and requires time for the final equilibrium to be reached. The experiments at first performed were run just long enough to give a definite permanganate color all through the electrolyte. Then on standing for a time (usually over night), it was found to be green in the morning. The explanation for this is that the amount of permanganate in the electrolyte was relatively small, that the solution was still strongly alkaline, and that the reducing reaction had not come to equilibrium. Although the concentration of the organic or reducing agents was low, it was still effective, and therefore required time to come to complete equilibrium with the final production of the green manganate. Furthermore, it is more than likely that the introduction of organic dust particles from the air aided in some measure, but this is not such a tremendously important factor, and is effective only when the solution is extremely alkaline.

An experiment was tried to prove this explanation, *i. e.*, that if the permanganate were present in sufficient concentration, it could not be reduced to manganate on standing for a short time. A 10 percent solution of sodium hydroxide was

taken with ferromanganese as anode and a platinum wire cathode as before, and a current of 1.25 amperes was passed through the electrolyte for six hours. The usual phenomena were observed—permanganate formed at anode, reduction to manganate on diffusion, and the gradual disappearance of the manganate as the electrolysis progressed. On breaking the circuit, the solution was so deeply colored by permanganate that its color could not be judged by transmitted light. This solution was left over night, and in the morning it was still colored with permanganate, and, although still strongly alkaline, the permanganate color persisted for four days. This solution was allowed to stand in an open beaker, which seems to show that the greatest part of the organic or reducing agents were removed from the electrolyte, and that the permanganate was reduced only very slowly by the organic dust particles.

The conditions of concentration and current strength have been taken up, and it has been shown that neither have any effect on the production of permanganate, so it was decided to try the effect of temperature. The higher temperatures are especially favorable to the formation of manganese compounds of a lower valency. As an instance, when a salt of manganese, the valence of which is less than six or, according to Ostwald, of any valence, is fused with K_2CO_3 or KOH and KNO_3, the manganese is oxidized to K_2MnO_4, and not $KMnO_4$. In this fusion, as in the case at hand, it is alkaline conditions with which we are dealing, although the results are different, for in one case manganate and in the other permanganate is found. While the temperature difference between the fusion and 95° (at which temperature the electrolysis was carried on) is wide, still it serves as an indication of the way in which the electrolysis might be expected to go at the latter temperature, 95°. The electrolysis of both the dilute and concentrated electrolytes with both current strengths, even though the electrolyte was first made pink with permanganate, gave the green manganate after running about half an hour. The beaker was covered with glass, the thermometer in the

electrolyte preventing complete covering, but the vapor issuing from the beaker would greatly reduce the possibility of the introduction of organic matter from the air, which, moreover, has been shown to be of minor importance in *rapid* reduction. At this temperature, 95°, there is a strong tendency to form ferrates, especially with the concentrated solution. It was thought at first that the reduction might be due to the reduction of the ferrates to ferrites by hydrogen at the cathode. Against this supposition, Haber and Pick have observed that the amount of this reduction is trifling. However, that there is dissolved iron present in the solution is indicated by the fact that iron is precipitated on the cathode. This iron is also noted in the cold solution, but no reduction of the permanganate takes place. Analysis of the electrolyte after reduction had taken place showed iron, and, furthermore, analysis of the sodium hydroxide used as electrolyte also showed iron. It is therefore not safe to conclude that the reduction is due to the formation of ferrates, which are reduced to ferrites by hydrogen for three reasons:

First—According to Haber and Pick, the amount of reduction from ferrate to ferrite is small.

Second.—Iron is precipitated on the cathode at both 95° and at room temperature, yet no reduction is noted in the solutions at room temperature.

Third.—The electrolyte contains iron *before* as well as after the electrolysis.

The reduction, then, must be due directly to the hydrogen at the cathode. This can be proved as follows: A porous cup was boiled out in alkaline solution of permanganate to rid it of reducing agents, then with dilute hydrochloric acid, to rid the pores of manganese dioxide, and finally, again with dilute alkaline permanganate, to get rid of the acid. This cup was then made the cathode compartment of a cell which contained a 2 percent solution of sodium hydroxide, made pink with permanganate and heated to 95°. The cathode was a platinum wire, the anode was ferromanganese, as before, and a current of 1.25 amperes was used. The solution in the cup was re-

duced to manganate in less than eight minutes. The electrodes were then reversed—the ferromanganese anode being placed in the cup (the solution in cup was still green) and the platinum cathode placed outside. In sixteen minutes, there was complete reduction to manganate, more time being required because the amount of solution was greater. The electrodes were again reversed, cathode now in the cup, and in about seven minutes the reduction was complete. The electrodes were then reversed again, with the result that reduction took place in a few minutes. This shows that the reduction is due to the hydrogen at this temperature. Furthermore, it was found that hydrogen from a Kipp easily reduces an alkaline permanganate.[1] The reduction takes place slowly at room temperature, and much more rapidly when heated to boiling.

The equation for this reaction is represented as follows:

$$2KMnO_4 + 2KOH + H_2 = 2K_2MnO_4 + 2H_2O.$$

Thus it is seen that the chemical and electrochemical reactions are in strict accord.

Thénard[2] said that the reduction of permanganate to manganate took place only with an alkali which contained some oxidizable substance. When the solution was made pink before running the current through the electrolyte, no formation of a manganate was noticed. However, if to an alkaline solution of permanganate alcohol is added, the permanganate is immediately reduced to manganate, and the odor of aldehyde is apparent. If the reaction

$$2KMnO_4 + 2KOH = 2K_2MnO_4 + H_2O + [O]$$

is considered, it will be noticed that oxygen is given off. An experiment was tried to see whether or not this was the case. Some alkaline permanganate solution was placed in a cylinder, which was fitted with a rubber stopper, through which ran a glass tube, at the upper end of which was a Bunsen valve. The level of the liquid in the cylinder and tube was marked.

[1] Jones: Jour. Chem. Soc., 33, 95 (1878).

[2] Jour. prakt. Chem., 69, 58 (1856); Comptes rendus, 42, 382 (1856).

This cylinder has stood three months, is still highly colored with permanganate, and the levels have not changed. Furthermore, the cylinder was heated in a bath to 95°, and after cooling down, the levels were not altered. These results show that under these circumstances a gas is not given off.

In the electrolysis it was noted that a large quantity of gas was evolved at the anode and it was therefore suspected that the efficiency was low. On testing, the maximum efficiency found was only 12 percent. To determine the amount of permanganate formed, the electrolyte was made acid by adding H_2SO_4 and then titrated with standard oxalic acid.

An attempt was made to ascertain the manner in which the permanganate was formed from the manganese. Is a hydroxide or oxide formed first and then oxidized to the permanganate? If manganese precipitated on copper from concentrated $MnCl_2$, is made anode in sodium hydroxide the manganese forms permanganate at once with a current of 250 milliamperes. With a current of 50–75 milliamperes the permanganate is formed very slowly and with a current of 5 milliamperes no permanganate is visible until such a current has run for twelve hours. On the other hand with ferromanganese as anode, permanganate is formed at once with all current strengths.

On exposure to the air the freshly deposited manganese becomes coated with a film of oxide or hydroxide. This hydroxide cannot be oxidized electrolytically to permanganate. If $Mn(OH)_2$ is spread over a platinum or nickel electrode and is made anode in sodium hydroxide it oxidizes to the black MnO_2 when a current of 2 or 3 amperes is passed through the electrolyte and no further oxidation is noted. Furthermore, if a piece of MnO_2, suspended by winding a platinum wire around it, is made anode in sodium hydroxide no further oxidation occurs either at room temperature or at 120° with two current strengths of 3 or 14 amperes. The same thing holds whether a $2^1/_2$ or a 50 percent solution of sodium hydroxide is used as electrolyte and also when a very small

amount, 50 milliamperes, is passed through the 2½ percent electrolyte for ten hours.

The normal reaction between manganese and caustic soda involves the formation of manganous hydroxide. When the current density is raised sufficiently, the formation of manganous hydroxide and of permanganate goes on simultaneously. Ferromanganese has practically no tendency to decompose water or caustic soda solution and therefore the only reaction is the formation of permanganate. The permanganate formed when manganese is made anode for a long time with a low current density cannot come from the manganous hydroxide. The last portions of the manganese to dissolve must therefore be in a different state from that which dissolves first. The last portions of the manganese to dissolve are those in immediate contact with the copper wire and it is probable that we have here a slight formation of cupromanganese, analogous to the formation of the zinc-platinum alloy when zinc is precipitated upon a platinum cathode. Special experiments with cupromanganese, showed that it behaves like ferromanganese and forms permanganate even with low current densities.

From the results of some preliminary experiments made on the action of sodium hydroxide on permanganate, it was decided to try the effect of various amounts of sodium hydroxide, colored with permanganate, on various amounts of permanganate.

A series of sixteeen beakers was made up of 150 cc mixtures of the alkali and permanganate. The alkali was a 10 percent solution, and the permanganate a 0.1 percent solution. The first beaker had 5 cc of the alkali and 145 cc of the permanganate. The number of cubic centimeters of permanganate was decreased by 10 cc steps, beginning with 140 cc, and the alkali increased by like amounts, until the number of cubic centimeters of sodium hydroxide reached 140 cc, then the increase and decrease was reduced to 5 cc. Thus the first beaker contained 145 cc of permanganate and 5 cc of sodium hydroxide; the second, 140 cc of permanganate and 10 cc of

sodium hydroxide; the third, 130 cc of permanganate and 20 cc of sodium hydroxide, and so on down, until the next to last contained 10 cc of permanganate and 140 cc of sodium hydroxide, and the last 5 cc of permanganate and 145 cc of sodium hydroxide. Under these circumstances, it may be inferred that any reduction to the manganate is due almost entirely to the introduction of organic matter from the atmosphere. The first to change was the one containing the 145 cc of sodium hydroxide, and the change was noticed six days after the experiment was started. The second to become green was the one containing 140 cc of sodium hydroxide, which turned green eight days after beginning the experiment. Owing to the fact that the solutions are standing in open beakers, the amount of evaporation is large, and the concentration is therefore changing. The evaporation is uniform, however, so the relative concentration is not changed. At points where the solid has crept up the sides, a reduction is noted, and is due, no doubt, to the better chance which the more concentrated solution has of attracting the dust particles.

At the end of three months it was found that the order in which the alkaline solutions of permanganate changed to the manganate followed exactly the order of increase in the alkalinity, the more alkaline solutions being the first to change. However, the first four beakers containing respectively 145 cc of $KMnO_4$ and 5 cc of alkali; 140 cc of $KMnO_4$ and 10 cc of alkali; 130 cc of $KMnO_4$ and 20 cc of alkali; and 120 cc of $KMnO_4$ and 30 cc of alkali are still pink. These four beakers have stood three months already and are still pink although some manganese hydroxide has precipitated out on the glass, indicating a slight reduction. This shows conclusively that the reduction in alkaline solutions depends on two factors—the alkalinity and amount of reducing material present.

Another experiment was tried to show the effect of surface exposed on the rate of reduction. A solution of known strength of permanganate was treated with a known quantity of 10 percent sodium hydroxide (which had been made pink with permanganate) and divided into two equal portions.

One of these portions was placed in a beaker and the other in a crystallizing dish, the ratio of the surface exposed being 1 to 14. The solution in the crystallizing dish was reduced in less than a day, while the solution in the beaker is still unchanged at the time of writing. This is another striking instance of the effect of organic dust in reducing, also the effect of increasing concentration. These results seem to indicate that the dust from the atmosphere will reduce, if given sufficient time, especially if acting in a concentrated solution.

What then can be said of the reaction:

$$2KMnO_4 + 2KOH = 2K_2MnO_4 + H_2O + [O].$$

At room temperatures and temperatures up to 95°, with a concentration at the start of 10 percent, sodium hydroxide, permanganate is not reduced by sodium hydroxide which is free from organic or reducing agents. When reducing agents are present, no gas is evolved, because the oxygen immediately combines with the reducing agent. Therefore, working within the concentrations stated, it is safe to say that the above equation does not represent the true state of affairs—the permanganate is not reduced to manganate by sodium hydroxide alone, and that even when reduction does occur no gas is evolved. The above statement holds only for the concentrations and temperatures mentioned.

1. Permanganate is formed at both concentrations of alkali used (2 and 10 percent), irrespective of the current strengths (0.25 and 1.25 amperes).

2. At 95°, it is reduced by hydrogen to the green manganate.

3. Any reduction at ordinary temperatures is due to reducing agents in the electrolyte.

4. Metallic manganese reacts with sodium hydroxide to form manganous hydroxide in the absence of a current or when the current density is low; but forms permanganate at higher current densities.

5. Manganous hydroxide can readily be oxidized electrolytically to manganese dioxide but not to permanganate.

The electrolytic formation of permanganate is therefore a direct reaction, not involving manganous hydroxide or manganese dioxide as intermediate steps.

6. The chemical and electrochemical results are in perfect accord.

The work was suggested and carried out under the direction of Professor Bancroft.

Cornell University.

NEW BOOKS

Notes on Electrochemistry. *By F. G. Wiechmann. 14 × 21 cm; pp. vi + 145. New York: McGraw Publishing Company, 1906. Price: bound, $2.00 net.*—The subject is discussed under the headings: general principles; electrical energy; electrochemistry; electrolytic dissociation; electro-analysis; electrotechnology. It is really surprising how much the author has presented in the space at his disposal. Under electrotechnology he touches on the Siemens and Halske, and the Hoepfner methods for extracting copper from its ores; on the multiple and the series system for refining copper; on the Moebius process for refining silver; on the electrolytic recovery of gold from cyanide solutions and on the Wohlwill process for refining gold; on the Betts process for lead; on the Browne process for nickel; on the Goldschmidt process for tin scrap; and on the various electrolytic zinc processes. Reference is made to the manufacture of caustic soda, hypochlorites, chlorates, and perchlorates; of calcium carbide, graphite, carborundum, siloxicon, and carbon bisulphide; of aluminum, sodium, phosphorus, steel, etc. Electroplating receives attention and under electrolytic analysis mention is made of the rotating anode and of the rotating cathode.

There are a few misprints: "Joules represent watts per second," p. 20; 30,000 amperes in the Kjellin furnace, p. 122; 2700° for the formation of siloxicon, p. 131. The Atmospheric Products Co., p. 128, has stopped work. Richards, Collins and Heimrod, p. 32, did not determine the electrochemical equivalent of silver. The voltaic series of the elements, p. 47, is misleading when given without more explanation.

Wilder D. Bancroft

Jahrbuch der Elektrochemie und angewandten physikalischen Chemie. *Berichte über die Fortschritte des Jahres 1904. Herausgegeben von Heinrich Danneel. XI. Jahrgang. 16 × 24 cm; pp. xii + 937. Halle: Wilhelm Knapp, 1906. Price: paper, 28 marks.*—This new volume keeps up to the standard set by the preceding ones. The change from electrochemistry to applied physical chemistry seems to have been a good one. It is interesting to notice that the use of the rotating anode in electrolytic analysis still seems to involve theoretical difficulties, 515.

Wilder D. Bancroft

Anleitung zum Gebrauch des Polarisationsmikroskops. *By Ernst Weinschenk. 14 × 22 cm; pp. vi + 147. Freiburg im Breisgau: Herdersche Verlagshandlung, 1906. Price: bound, $1.25 net.*—The chemist will find this little book just what he needs. All chemists should use the microscope a great deal more than they do. One reason for this failure to make use of a valuable tool is ignorance of its possibilities. While this volume is written primarily for the crystallographer, the chemist can derive a great deal of good from it.

Wilder D. Bancroft

ELECTROLYTIC PRECIPITATION OF BRONZES

BY B. E. CURRY

It is commonly supposed that it is difficult to precipitate good bronze electrolytically. For this reason the general method for preparing bronze plate is to precipitate a brass and bronze it by chemical methods.[1]

The best brass is precipitated from cyanide solutions. Because of the slight solubility of the cyanide of tin this solution can not be employed for the deposition of bronze.

Brass cannot be precipitated satisfactorily from ordinary salt solutions. The tendency for the copper to precipitate first causes the solution to concentrate continually with respect to the zinc and at the same time to become poor in copper. When the ordinary salt solutions of copper and tin are electrolyzed the copper precipitates first and the solution becomes rich in tin. For this reason the more common electrolytes cannot be used for a continuous precipitation of bronze.

Since the ordinary salt solutions are not satisfactory for the deposition of bronze it was thought advisable to try some solution in which both copper and tin form soluble double salts. In selecting an electrolyte the behavior at the anode as well as at the cathode must be considered. It has already been shown that over a considerable range the bronzes dissolve quantitatively[2] in both alkaline tartrate and acid ammonium oxalate solutions.

Some tests with the alkaline tartrate solutions showed these to be undesirable. A satisfactory bronze could not be obtained and the solution changed continually in concentration. In the presence of the stannous salts the copper was thrown from solution and deposited on the walls and bottom of the containing vessel. For these reasons the tartrate solution was abandoned.

[1] Watt and Philip: Electroplating of Metals, 308.

[2] "Electrolytic Corrosion of the Bronzes," Jour. Phys. Chem., 10, 487.

Some preliminary tests with acid ammonium oxalate solutions produced a good bronze. Experience has shown that this solution must be prepared with a considerable amount of care. If the acid content is made too high, the copper is precipitated as an insoluble salt. When the acid content is too low or the solution slightly alkaline, the tin becomes insoluble. At ordinary temperatures about 7 percent oxalic acid forms a saturated solution; the ammonium salt is a little less soluble.

It was noted early in the work that there was a wide difference between the composition of the deposited bronze and the relative amounts of copper and tin in solution. In order to determine the composition of the solution and that of the bronze the following stock solutions were prepared:

Grams $H_2C_2O_4$	Grams $(NH_4)_2C_2O_4$	Grams $CuSO_45H_2O$	Grams SnC_2O_4	cc H_2O
5	55	—	18	1000
5	55	15	—	1000

From these, two series of solutions were made up with known amounts of copper and tin varying in shifts of 10 percent. It will be noted that these solutions are different from the solutions in which the corrosion experiments were made inasmuch as they contain sulphates. The presence of sulphates or chlorides is necessary in order to keep the copper in solution. One of these series was electrolyzed with a 90 percent copper anode and the other with an 80 percent anode. In each case about 0.3 gram of bronze was deposited, weighed, and then analyzed. The anodes were weighed before and after each run. In this way a check was had on the composition of the solution at the end of the run. In runs of this length the total change in the concentration of the copper and tin in solution was not great. Corrections were calculated for this and the results plotted in Fig. 1. Here the coordinates are percentage copper in solution and percentage copper in the precipitated bronze. As the curve indicates that there is a wide

difference between the composition of the solution and of the precipitated bronze, the curve also indicates that the lowest copper content an electrolytic bronze can have is about 78 percent. However, when a 75 percent copper anode is used a fairly good bronze with 75 percent copper content can be

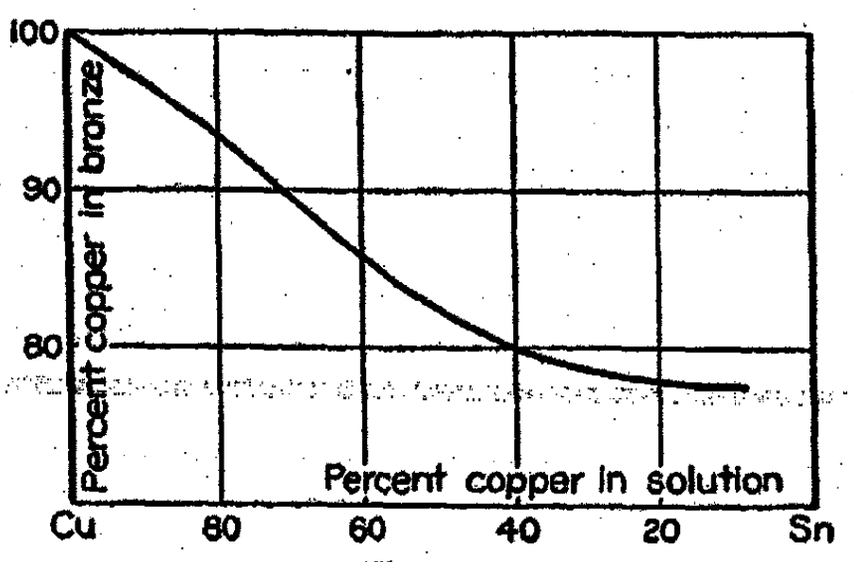


Fig. 1

obtained. When the copper content in solution becomes as low as 10 percent of the total amount of copper and tin in solution some care is necessary to prevent the deposit from becoming black and spongy. Also the composition is likely to vary.

In these runs the anodes were cast in the form of plates with a surface on one side of about 40 cm^2. The cathodes were platinum discs with a surface of 30 cm^2. The cathodes were rotated and in this way the solutions kept well stirred and the deposit remained bright and smooth. If the solutions are not stirred the deposits blacken very quickly. If the anodes remain stationary there is some tendency for slimes to form but this is not great.

In order to show more conclusively that the curve in Fig. 1 represents the facts obtained in longer runs, solutions containing relatively 82.5 percent, 70 percent and 60 percent copper were electrolyzed with 95 percent, 90 percent and 85 percent copper anodes respectively. The anode density was 0.3 ampere per dm^2 and the cathode density 0.2 ampere per dm^2. In this case the cathodes were cast in the form of cyl-

inders and both cathode and anode were rotated. At the end of the run both the anode and cathode were bright and clean. The results are given in Table I.

TABLE I

Percent Cu in anode	Percent Cu in solution	Anode loss in grams	Wt. of bronze in grams	Percent Cu in bronze
95	82.5	3.44	3.51	94.7
90	70.0	2.70	2.52	89.5
85	60.0	3.08	2.90	86.5

At the end of the runs about 0.3 gram of the bronze was deposited on clean electrodes and analyzed. In the solutions which were electrolyzed with 95 percent and 90 percent copper electrodes the solutions were practically unchanged. The 85 percent anode became tin-rich on the surface and for this reason the concentration of the solution and deposited bronze shifted slightly. The bronzes with a copper content varying between 74 percent and 87 percent are composed of two phases, the α-phase rich in copper and the δ-phase rich in tin. In oxalate solutions containing sulphates the α-phase tends to dissolve first and the surface of the anode becomes rich in δ-crystals. Between 87 percent and pure copper the bronzes have but one form of crystallization and dissolve uniformly without change.

A second series of runs was made with copper chloride substituted for the copper sulphate in the original solution. The chlorides do not interfere with the cathode reaction in any way. The results are given in Table II.

TABLE II

Percent Cu in anode	Percent Cu in solution	Anode loss in grams	Weight of bronze in grams	Percent Cu in bronze
85	60	2.01	2.37	85.5
80	49	2.38	2.00	81.2

These anodes dissolve without change and the tendency to dissolve tin-rich did not appear as in the solutions containing sulphates.

In these longer runs the deposits remained bright but became rough and pitted toward the end.

Some experiments were made with a high current density at the anode to determine the effect on the solubility. With a current density of one ampere per square decimeter the anodes containing more than 87 percent copper dissolved uniformly and with a good efficiency. With less than 87 percent copper at the higher current densities the tendency for the anodes to become tin-rich was more apparent. The current density at the cathode can vary over a considerable range and the deposit remain satisfactory. Good deposits were obtained with a current density varying from 0.2 ampere to 2 amperes per square decimeter.

When cast bronzes with more than 87 percent copper are annealed below 500° C they are homogeneous under the microscope. There is but one form of crystallization over this range. These crystals are designated as α. The bronze with 74 percent copper is also homogeneous and this particular form of crystallization is designated as δ. Over the range between 74 percent and 87 percent copper the bronzes are not homogeneous but show a mixture of α- and δ-crystals.

It is certain that the electrolytic bronzes are deposited under equilibrium conditions. All of these appear homogeneous under the microscope when the copper content is above 90 percent. The 76 percent copper bronze is almost homogeneous but there is evidence of a small amount of a second phase. The 83 percent bronze shows two phases in almost equal amounts.

The electrolytic bronzes with more than 88 percent of copper bend readily, but with a less amount of copper the bronze begins to harden and break when bent. These do not dissolve readily in nitric acid. The electrolytic bronzes correspond closely in color and general appearance to the cast bronzes over the same range of composition.

The best plating solution for bronzes should contain about 5 grams of free oxalic acid and 55 grams of ammonium oxalate per 1000 cc of water. The relative amounts of copper and tin in solution may be shifted in any ratio depending on the composition of the plates desired. The cathode should be rotated if possible.

The presence of chlorides is preferable to large amounts of sulphates.

It has been found to be very difficult to precipitate a good bronze with less than 75 percent copper content.

A low current density at the cathode is necessary.

The anode dissolves better when rotated.

The electrolytic bronzes represent equilibrium conditions.

This work has been carried on under a grant from the Carnegie Institution to Professor Bancroft.

Cornell University, May, 1906.

NOTE ON AN EXTENSION OF THE THEORETICAL APPLICABILITY OF GULDBERG AND WAAGE'S MASS LAW

BY T. BRAILSFORD ROBERTSON

(From the Rudolph Spreckels Physiological Laboratory of the University of California)

It is frequently stated[1] that the Guldberg and Waage mass-equation can only be applied with a theoretical basis to systems which obey the gas law PV = RT. It can, however, be shown I think, that this is too narrow a conception of the scope of the Guldberg and Waage law. The derivation of the mass-law from the gas-laws according to Larmor[2] is briefly as follows:

The increase in free energy due to the appearance of new molecules or atoms during a chemical change will involve two terms, one expressing the work a done in forming the particle at the temperature chosen and at a standard pressure, and another giving the work required to bring, isothermally, the new substance, when formed, to the pressure of the system. If the system obeys the law PV = RT, the work done in an isothermal change from P to P_0 is $\int_P^{P_0} P dv$ and since $v = \frac{RT}{P}$, $\delta v = \frac{-RT}{P^2}\delta p$, so that the expression for the work becomes:

$$\int_{P_0}^{P} \frac{RT}{P} dP = RT \log_e \frac{P}{P_0}.$$

Thus the change in the available energy of the system is $a + RT \log_e bc$, where a is a function of the temperature T,

[1] For instance, van't Hoff. Lectures on Theoretical and Physical Chemistry, Trans. by Lehfeldt, p. 195. L. Michaelis: Biochem. Centr. 3, 1.

[2] Larmor: Phil. Trans., 190A, 276 (1887).

R is the gas constant per gram-molecule, c is the final number of molecules of the given species per unit volume and b is a constant expressing the dilution of the molecules at the standard pressure and the given temperature. When equilibrium is reached, the change of available energy arising from a further slight chemical change must vanish so that at equilibrium we have:

$$n_1(a_1 + RT \log_e b_1c_1) + n_2 (a_2 + RT \log_e b_2c_2) + \ldots . = 0$$

or

$$RT(\log b_1^{n_1}b_2^{n_2} \ldots + \log C_1^{n_1}C_2^{n_2} \ldots) = -(n_1a_1 + n_2a_2 + \ldots)$$

where $n_1, n_2 \ldots$ are the numbers of the molecules of the different types which are involved in the reaction, reckoned positive when they appear, negative when they disappear.

Hence we obtain:

$$C_1^{n_1}C_2^{n_2} \ldots . = K$$

which is the generalized expression of the mass-law.

The extension of this principle which I wish to point out is, however, as follows: If the system obeys, not the simple law $PV = RT$, but a law expressed by the equation $P(V-d) = RT$, where d is a constant, then, as before, the work done by an isothermal change from P to P_o is $\int_P^{P_o} P dv$ and, since $v = \frac{RT}{P} + d$, $\delta v = \frac{-RT}{P^2}\delta P$ as before, so that, as in the simpler case, the expression for the work is:

$$\int_{P_o}^{P} \frac{RT}{P} dP = RT \log_e \frac{P}{P_o}$$

and, following the same train of reasoning, we regain the mass law:

Hence the mass law in its simple form holds good for all systems in which $P(V-d) = RT$.

Now Ostwald,[1] Bredig,[2] and Noyes[3] have shown that the formula $P(V - d) = RT$ holds good for a variety of solutions and much more closely than the formula $PV = RT$. It does not appear impossible that the same formula will be found to express the relations between osmotic pressure, volume, and temperature in the majority of systems with which the biochemist has commonly to deal. It would indeed be strange if the mass equation were so limited in its application as the statements to which I have referred would lead us to suspect, since it is known to hold good in concentrated solutions[4] to which the formula $PV = RT$ does not even approximately apply.

[1] W. Ostwald: Zeit. phys. Chem., 2, 280 (1888). See also, Solutions. translated by Pattison Muir (1891), p. 237.

[2] Bredig: Ibid., 4, 444 (1889).

[3] Noyes: Ibid., 5, 53 (1890).

[4] For instance, in the formation of ethyl acetate from acetic acid and ethyl alcohol where the only water in the system is that produced by the reaction. Berthelot and Pean de St. Gilles: Ann. Chim. Phys., 65, 385 (1862); 66, 5 (1862); 68, 225 (1863); van't Hoff: Ber. chem. Ges., Berlin, 10, 669 (1870)

ON THE CONDITIONS OF EQUILIBRIUM OF AN ASSOCIATING AMPHOTERIC ELECTROLYTE IN THE PRESENCE OF ANY NUMBER OF NON-AMPHOTERIC ELECTROLYTES.

BY T. BRAILSFORD ROBERTSON

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I. Introduction

The question of the conditions of equilibrium of amphoteric electrolytes is one of especial interest to biologists. The chemical entities with which they have generally to deal are of a protein nature and there can be little doubt that the proteins belong to the class of amphoteric electrolytes.

That protein salts are electrolytes, that is, that they ionize in aqueous solution, has been especially pointed out by Mann[1], Billitzer[2], Freundlich,[3] Laqueur,[4] and Hardy,[5] while attention has been drawn to the amphoteric nature of proteins by Strecker,[6] Bredig,[7] Winkelblech,[8] Walker,[9] Hardy[10] and Mann;[11] the researches of Hammarsten,[12] Söldner,[13] Courant,[14]

[1] Gustav Mann: "Physiological Histology" Oxford (1902), p. 45. "Chemistry of the Proteids" (1906), 259, 268.

[2] J. Billitzer: Drude's Ann., 316, 902 and 937 (1903).

[3] H. Freundlich: Zeit. phys. Chem., 44, 129 (1903).

[4] Laqueur: Dissertation, Breslau, 1905; Biochem. Centr., 3, 670.

[5] W. B. Hardy: Jour. of Physiol., 33, 251 (1905).

[6] Strecker: Liebig's Ann., 148, 87 (1886).

[7] Bredig: Zeit. Elektrochemie, 6, 33 (1899).

[8] Winkelblech: "Über amphotere Elektrolyte und innere Salze," Leipziger Dissertation, 1901, quoted after Mann, "Chemistry of the Proteids," 1906, p. 208; Zeit. phys. Chem., 36, 546 (1901).

[9] Walker: Zeit. phys. Chem., 49, 82 (1904).

[10] W. B. Hardy: l. c.

[11] Gustav Mann: "Chemistry of the Proteids" 1906, pp. 145 and 208.

[12] Hammarsten: Maly's Jahres. Thierchem., 4, 146 (1874).

[13] Söldner: Landwirthsch. Versuchsstation, 35, Separat 18, quoted after Hammarsten "Text-book of Physiological Chemistry," translated by Mandel, 4th ed. (1904), p. 441; Jahresber. Anat. und Physiol., 17, 314.

[14] Courant: Pfluger's Arch. f. d. ges. Physiol., 50, 109 (1891).

Sjöqvist,[1] Cohnheim,[2] Spiro and Pemsel,[3] Bugarszky and Liebermann,[4] Ley,[5] T. B. Osborne,[6] Cohnheim and Krieger,[7] Maas,[8] Erb,[9] W. A. Osborne,[10] Sackur,[11] von Rhorer,[12] Sollmann,[13] Volhard,[14] Laqueur and Sackur,[15] van Slyke and Hart,[16] Long,[17] Hardy,[18] and Mellanby,[19] having shown that proteins react as bases towards acids and as acids towards bases. This probably, taken in conjunction with other evidence, indicates a structure similar to that of Fischer's polypeptids.[20] On the other hand, the difficulties which have been met with in the attempt to apply the ordinary physico-chemical laws, such as obtain in systems containing only dilute non-amphoteric electrolytes, to systems containing proteins have proved very great. The researches of W. B. Hardy on globulin[18] and those of Bugarszky and Liebermann[4] on albumin

[1] Sjöqvist: Skandinav. Arch. f. Physiol., 5, 277 (1894) where the older literature on the compounds of proteins with acids will be found collected. Ibid., 6, 255 (1895).

[2] O. Cohnheim: Zeit. Biol., 33, 489 (1896).

[3] Spiro and Pemsel: Zeit. physiol. Chem., 26, 233 (1898).

[4] Bugarszky and Liebermann: Pflüger's Arch. f. d. ges. Physiol., 72, 51 (1898).

[5] Ley: Zeit. phys. Chem., 30, 193 (1899).

[6] T. B. Osborne: Jour. Am. Chem. Soc., 21, 486 (1899); Zeit. physiol. Chem., 33, 225-240 (1901).

[7] O. Cohnheim and Krieger: Zeit. Biol., 40, 485 (1900).

[8] Maas: Zeit. physiol. Chem., 30, 61 (1900).

[9] Erb: Zeit. Biol., 41, 309 (1901).

[10] W. A. Osborne: Jour. Physiol., 27, 398 (1901).

[11] Sackur: Zeit. phys. Chem., 41, 679 (1902).

[12] von Rhorer: Pfluger's Arch. f. d. ges. Physiol., 90, 368 (1902).

[13] Sollmann: Am. Jour. Physiol., 7, 203 (1902).

[14] Volhard: Münch. med. Wochenschr. (1903), No. 50, Biochem. Centr. 2, 231.

[15] Laqueur and Sackur: Hofmeister's Beitr. Chem. Physiol. und Pathol., 3, 196 (1903).

[16] van Slyke and Hart: Am. Chem. Jour., 28, 411 (1902); 33, 461 (1905).

[17] Long: Journ. Am. Chem. Soc., 18, 382 (1906).

[18] W. B. Hardy: l. c.

[19] Mellanby: Jour. Physiol., 33, 338 (1905).

[20] Gustav Mann: "The Chemistry of the Proteids," p. 145.

and albumose have been successful in proving that these proteins combine with acids in molecular proportions, and those of Laqueur and Sackur and van Slyke and Hart, in the papers to which I have referred, have shown that casein combines with bases and acids in equivalent-molecular proportions; although it must be remembered that hydrolytic dissociation plays a great part in the equilibrium finally obtained.[1] The attempts to formulate a mass relationship between salts and proteins have, however, met with great difficulties. Thus Galeotti[2] and Guerrini[3] find that when protein is precipitated by salts the proportion of salt to protein in the precipitate varies continuously, while Spiro[4] and Freundlich[5] deny that the precipitation of proteins by salts is a truly chemical phenomenon, although Freundlich admits that chemical factors may be involved. Not even in the case of salts of the heavy metals is there any constant proportionality between the concentration of the salt and the amount of protein precipitated[6]. Hardy, however, considers that compounds between globulin and salts are formed but that they are stable only when their dissociation is completely suppressed by excess of salt.[7] Recent observers agree in stating that the rate of hydrolysis of proteins by pepsin, trypsin, and erepsin is proportional

[1] Erb : l. c. ; Arrhenius and Ley : Zeit. phys. Chem. (1899) ; 30, 193 (1899) ; Bugarszky and Liebermann : l. c.; Spiro and Pemsel : l. c.; Laqueur : "Über das Kasein als Säure und seine Unterschiede gegen das durch Lab veränderte (Parakasein) Theorie der Labgerinnung" Dissertation, Breslau, 1905. Biochem. Centr., 3, 670.

[2] Galeotti : Zeit. physiol. Chem., 40, 492 (1904) ; 44, 461 (1905).

[3] Guerrini : Ibid., 47, 287 (1906).

[4] Spiro: Hofmeister's Beitr. Chem. Physiol., 4, 300 (1903).

[5] Freundlich : Zeit. physiol. Chem., 44, 120 (1903).

[6] Galeotti : Zeit. physiol. Chem., 40, 492 (1904) ; W. Pauli : Hofmeister's Beitr. chem. Physiol., 6, 233 (1905). See also table of percentages of heavy metals combined with protein found by different observers. Gustav Mann : "Chemistry of the Proteids," 1906, p. 306.

[7] W. B. Hardy : l. c.

to the amount of ferment present,[1] as would be expected if the enzyme acted upon the substrate through the formation of an intermediate compound according to Guldberg and Waage's mass law. But this proportionality only holds good within circumscribed limits of substrate, enzyme, and hydrion or hydroxidion concentration.[2] My own experiments upon the hydrolysis of casein by trypsin[3] enable me to confirm these statements. On the other hand, some consider that the velocity of the action between substrate and enzyme in these cases is not to be referred primarily to chemical mass action.[4]

In another field, that of toxins and anti-toxins and of allied substances, the Guldberg and Waage mass law has been applied with considerable success, particularly by Arrhenius and Madsen;[5] nevertheless, objections have been raised, and Michaelis, in particular, has alluded to many instances which, he considers, do not conform to the principles enunciated by Arrhenius and Madsen,[6] and although many of these objec-

[1] For Pepsin:

Sjöqvist: Skand. Arch. Physiol., 5, 277; Sawjalow: Zeit. physiol. Chem., 46, 307.

For Trypsin:

V. Henri and Larguier des Bancels: Comptes rendus, 136, 1099, 1581 (1903). A. E. Taylor; Univ. of California publications, Pathology, 1, 7 (1904). Bayliss: Arch. des Sciences Biol., 11, Supplt., p. 261 (1904). Reprinted in collected papers of the physiological laboratory of Univ. Coll., London, Vol. 13. S. G. Hedin: Journ. Physiol., 32, 468 (1905), and 34, 370 (1906).

For Erepsin:

Vernon: Jour. Physiol., 30, 334.

[2] Sjöqvist: l. c.; A. E. Taylor: l. c.; Bayliss: l. c.

[3] Shortly to appear.

[4] Herzog: Zeit. physiol. Chem., 41, 416; Dauwe: Hofmeister's Beitr., 6, 426 (1905).

[5] Arrhenius and Madsen: Zeit. phys. Chem., 44, 1 (1903); Madsen: Centr. f. Bakteriol., 34, 630 (1903), quoted after Biochem. Centr., 2, 120; Arrhenius: Zeit. phys. Chem., 46, 415; Madsen and Walbum: Centr. *f.* Bakteriol., 36, 2, 28 (1904); Biochem. Centr., 2, 731; Arrhenius and Madsen: Centr. f. Bakt., 36, 612; 37, 1 (1904); Biochem. Centr., 3, 256; Arrhenius: Zeit. Elektrochemie, 10, 661 (1904); Madsen: Acad. Roy. des Sci. et des Lettres de Danemark No. 1; Biochem. Centr., 3, 725; Madsen and Noguchi: Ibid., No. 6; Biochem. Centr., 3, 725.

[6] Michaelis: Biochem. Centr., 3, 1 (1904); Ibid., 3, 693 (1904). In these articles the previous literature on toxins and antitoxins, and on precipitins, will be found collected. See also, Biltz, Much and Siebert: Behring's Beitr. zur Exper. Ther. Heft. 10. Biochem. Centr., 3, 724; Nernst: Zeit. Elektrochemie, 10, 377 (1904); J. A. Craw: Jour. Hygiene, 5, 113; Biochem. Centr., 3, 680; Zeit. phys. Chem., 52, 569; Proc. Roy. Soc., 76 B, 179 (1905).

tions doubtless rest upon misconceptions, such as an unjustifiable limitation of the applicability of Guldberg and Waage's mass law,[1] or upon such assumptions as that dilution of a colloid does not alter its active mass,[2] an assumption depending upon an arbitrary distinction between colloids and crystalloids which, recollecting the fact that many colloids are electrolytes, must be considered untenable, we may nevertheless consider it highly probable that the principle of Guldberg and Waage's law mass can only be applied in a direct manner to the toxin-antitoxin reactions, as to the ferment reactions and the other protein reactions which we have discussed, under certain definite conditions. Nevertheless, all the instances which we have reviewed in which the ordinary physico-chemical laws governing the interaction of dilute non-amphoteric electrolytes undoubtedly do hold good cannot be due to mere accident; far less can they be devoid of theoretical foundation as some authors have hinted. Rather do the facts appear to indicate that those instances in which the simple laws hold good are particular cases, under limiting conditions, of more general laws.

In this connection it occurred to me that many of the difficulties encountered in applying physico-chemical laws to protein systems might possibly be attributed to the insufficient consideration of the amphoteric nature of proteins and the manner in which the ordinary conditions of equilibrium are thereby modified.

The conditions of equilibrium of a non-associating amphoteric electrolyte in the absence of other electrolytes have been discussed by Walker[3] and he has pointed out how in many respects the equilibrium conditions differ from those which can be applied to non-amphoteric electrolytes. Assuming that the amphoteric electrolyte HXOH does not associate to form molecules of the type HXX....OH or of the type XX... but

[1] I have considered this in the note which precedes this paper.

[2] J. A. Craw: Proc. Roy. Soc., 76 B, 179 (1905).

[3] J. Walker: Ibid., 73, 155 (1904); Zeit. phys. Chem., 49, 82 (1904); Proc. Roy. Soc., 74, 271 (1904).

forms "internal salts"[1] of the type $\begin{matrix} R.NH_3 \\ | \quad | \\ COO \end{matrix}$ which can be represented by X, the conclusions arrived at by Walker can be represented as follows:

Let the active masses of the various substances for equilibrium be represented thus:

H^+	OH'	XOH'	HX^+	HXOH X
a	b	c	d	e

Then:

$$a^2 = K.\frac{K + k_a e}{K + k_b e} \quad \ldots\ldots(1) \qquad a = \frac{K}{b} \quad \ldots\ldots(1')$$

$$b = \frac{K}{a} \quad \ldots\ldots(2) \qquad b^2 = K.\frac{K + k_b e}{K + k_a e} \quad \ldots\ldots(2')$$

$$c = \frac{k_a e}{a} \quad \ldots\ldots(3) \qquad c = \frac{k_a e b}{K} \quad \ldots\ldots(3')$$

$$d = \frac{k_b e a}{K} \quad \ldots\ldots(4) \qquad d = \frac{k_b e}{b} \quad \ldots\ldots(4')$$

where K is the constant ionic product for water, which includes within it the constant active mass of water, k_a is the dissociation constant of the amphoteric electrolyte regarded as an acid and k_b is its dissociation-constant when it acts as a base.

It is evident, however, that the case considered by Walker is a simple one compared to that which we generally have to consider in a protein system. In the first place, investigations on the equilibria of protein systems are generally concerned with the influence of electrolytes or of other proteins upon the protein under consideration and Walker's equations do not supply the necessary data for a theoretical investigation

[1] Winkelblech: Zeit. phys. Chem., 36, 546 (1901).

[2] In Walker's papers the quantity which I have denoted by e is denoted by the symbol u and the active masses of HXOH and X are denoted by the separate symbols e and f, respectively. Since, however, the quantity which Walker designates f must always be proportional to that which he designates e, their sum must be proportional to e and I have utilized this symbol to denote this sum.

of such mixtures. In the second place, Walker's equations do not take into consideration the possibility of the formation of association compounds or of polymeric modifications of the amphoteric electrolyte such as undoubtedly occur in the case of proteins. The precipitate on neutralizing a solution of acid- or alkali-albumin and the great increase in opalescence on neutralizing a solution of a casein salt, to mention two well-known instances, point to the formation of large molecule-complexes or of pseudo-ions,[1] nor can we place any definite limit upon the number of different complexes of the type XXX ....which may be formed. Nor must we ignore the possibility of such complexes retaining their amphoteric character, as in the case of Fischer's polypeptids.[2]

I propose, therefore, to investigate, in this paper, the theoretical conditions of equilibrium in the following systems:

A. An association or polymerizing amphoteric electrolyte, the ions of which are all univalent, in the absence of other electrolytes.

B. An associating amphoteric electrolyte, the ions of which are univalent, in the presence of any number of non-amphoteric electrolytes, the ions of which are all univalent.

C. Two associating amphoteric electrolytes, the ions of which are univalent, in the presence of any number of non-amphoteric electrolytes, the ions of which are all univalent.

D. An associating amphoteric electrolyte, the ions of which are both divalent and univalent, in the presence of any number of non-amphoteric electrolytes, the ions of which are univalent.

E. An associating amphoteric electrolyte, the ions of which are all univalent, in the presence of any number of non-amphoteric electrolytes, the ions of which are partly univalent and partly divalent.

At the outset of such an investigation the question arises whether we are justified in applying the Guldberg and Waage

[1] W. B. Hardy: Jour. Physiol., 33, 257 (1905).

[2] See Gustav Mann: "Chemistry of the Proteids," p. 145 (1906).

mass law to the reactions between *individual pairs of ions* in such systems as the above. The considerations which I have put forward in the note which precedes this paper, together with the fact that the mass law can, under certain conditions, be directly applied to many protein systems justify us, I think, in adopting this procedure, at all events as a working hypothesis.

In concluding these introductory remarks I wish to define a few terms which I shall have occasion to use.

The term "*ampholyte*" will be used as a synonym for "amphoteric electrolyte."

I propose to call ampholytes of the types $\overset{+}{H} + XOH'$ and $HX + \overset{+}{OH}'$, *acid and basic ampholates* respectively, to distinguish them from their salts.

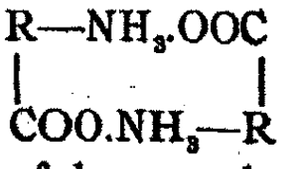
The simplest ampholate in a given system, represented by HXOH, I will designate the ampholate of the *first order*, those represented by HXXOH,....,HXX....OH, being designated ampholates of the *second...nth orders.* The compounds of an acid ampholate with a non-amphoteric base or of a basic ampholate with a non-amphoteric acid, will be termed "*ampho-salts.*"

An ampho salt formed by the substitution of a base for hydrogen in an acid ampholate can split off ions in either of two ways, either it can split into the ion which has replaced the hydrogen of the ampholate and an anion, or it can split into a cation and hydroxyl, thus, in the second instance, acting as a base, such ampho-salts will be termed *basic ampho-salts.* Similarly, the ampho-salt formed by the substitution of an acid radical for the hydroxyl of an ampholate can act as an acid, and such ampho-salts will be termed *acid ampho-salts.*

The compound of an acid ampho-salt with a basic ampho-salt, which can no longer split off hydrogen or hydroxyl ions, will be termed a "*di-salt.*"

The term "*internal salt*" due to Winkelblech, will, for the purposes of this paper, be restricted to substances of the

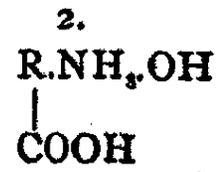
type  formed from the ampholate of the corresponding order by a modification of the internal structure.

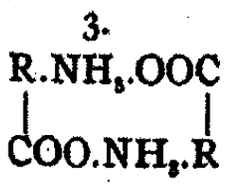
The term "*association-salt*" will be applied to substances of the type  formed by the combination of two ampholates of lower orders.

II A. The Conditions of Equilibrium of an Associating Ampholyte, the Ions of Which Are All Univalent, in the Absence of Other Electrolytes

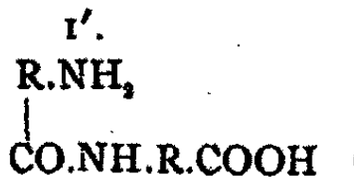
Allowing for the formation of internal salts, ampholates of various orders, association-salts etc., we have the following types of substances to deal with:

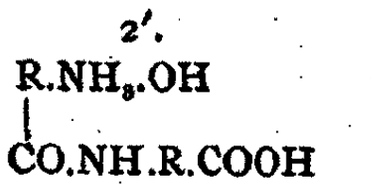
1. 

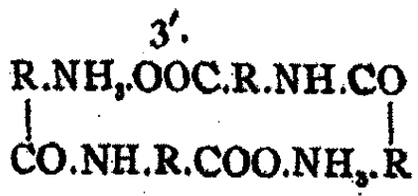
2. 

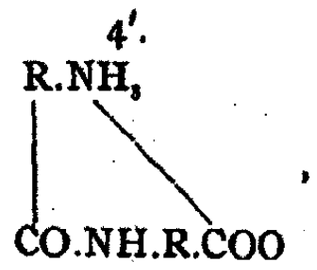
3. 

4. 

1′. 

2′. 

3′. 

4′. 

etc., and all the ions which can be derived therefrom, the polymerization being repeated indefinitely.

Now we are unable, by the methods which we shall use, to distinguish between the un-ionized isomeric forms 1 and 4, but since, by the law of mass action, they must always exist in the solution in invariable proportions we may, for our present purposes, regard them as one and the same substance.[1]

[1] See also Walker: Proc. Roy. Soc., 73, 156 (1904).

Thus in the scheme representing the various substances in equilibrium we shall not include the internal salts but only the types HXX....OH, and we shall represent the active mass of each ampholate + the corresponding internal salt by a single symbol e_n (the subscript denoting the order of the ampholate), always recollecting that if e'_n be the active mass of the ampholate of order n, $e_n = (1 + k)e'_n$, where k is the ratio of the velocity constants for the reaction of the type:

$$\begin{matrix} R.NH_2 \\ | \\ COOH \end{matrix} \rightleftharpoons \begin{matrix} R.NH_3 \\ | \\ COO \end{matrix}$$

Similarly, we are unable to distinguish between 1 and its hydrated form 2, but here, also, by the mass law, the two must be present in the solution in constant proportions.[1]

We may assume that the ions are derived from the hydrated form. The constant ratio between the hydrated and anhydrous forms will therefore appear in the velocity constants for the ion-reactions which give rise to the ampholates.

Let the active masses of the various substances for equilibrium, in the case under consideration, be represented as follows:

H^+	OH'	XOH'	$XX....OH'$	HX^+	$HXX....^+$	$HXOH$
a	b	c_1	c_n	d_1	d_n	e_1

$HXX....OH$	XX	$XX....X$
e_n	f_2	f_{2n}

XX...X denoting an association-salt. Since two ampholates of order n may combine to form an association salt, the total number of orders of association salts will be $2n-1$, but the most complex ampho-salt will contain $2n$ radicals of the type X and may therefore be denoted by f_{2n}. For equilibrium between the various positive and negative ions in pairs we have:

$$ab = K \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5)$$

[1] See also Walker: l. c.

$$\left.\begin{aligned} ac_1 &= k_a^{(1)} e_1 \\ &\cdots\cdots \\ ac_n &= k_a^{(n)} e_n \end{aligned}\right\} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (6)^1$$

$$\left.\begin{aligned} bd_1 &= k_b^{(1)} e_1 \\ &\cdots\cdots \\ bd_n &= k_b^{(n)} e_n \end{aligned}\right\} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (7)^1$$

$$\left.\begin{aligned} c_1 d_1 &= Q_1 f_1 \\ &\cdots\cdots \\ c_n d_m &= Q_{n+m} f_{n+m} \end{aligned}\right\} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (8)$$

and the sum of the concentrations of the positive ions must be equal to the sum of the concentrations of the negative ions, so we have:

$$a + d_1 + \ldots + d_n = b + c_1 + \ldots\ldots + c_n \ldots\ldots\ldots\ldots (9)$$

From (6) we have:

$$a(c_1 + \ldots\ldots + c_n) = k_a^{(1)} e_1 + \ldots + k_a^{(n)} e_n$$

$$\therefore \quad c_1 + \ldots\ldots + c_n = \frac{1}{a} \sum_{i=1}^{i=n} k_a^{(i)} e_{(i)} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (10)$$

Similarly:

$$d_1 + \ldots\ldots + d_n = \frac{1}{b} \sum_{i=1}^{i=n} k_b^{(i)} e_{(i)} \ldots\ldots\ldots\ldots\ldots\ldots\ldots (11)$$

Substituting from (10) and (11) in (9) we have:

$$a + \frac{1}{b} \sum_{i=1}^{i=n} k_b^{(i)} e_{(i)} = b + \frac{1}{a} \sum_{i=1}^{i=n} k_a^{(i)} e_i.$$

Multiplying both sides of the equation by $a^2 b$ we have:

$$a^2.ab + a^2 \sum_{i=1}^{i=n} k_b^{(i)} e_i = a^2 b^2 + ab \sum_{i=1}^{i=n} k_a^{(i)} e_i.$$

---

[1] Be it noted, again, that $k_a^{(n)}$, $k_b^{(n)}$, etc., in these equations are *not* the affinity constants for the acid and basic ampholates, but are respectively *proportional* to them.

Hence, from (5), we have:

$$a^2\mathrm{K} + a^2 \sum_{i=1}^{i=n} k_b^{(i)} e_i = \mathrm{K}^2 + \mathrm{K} \sum_{i=1}^{i=n} k_a^{(i)} e_i$$

$$\therefore \quad a^2 = \mathrm{K}. \frac{\mathrm{K} + \sum_{i=1}^{i=n} k_a^{(i)} e_i}{\mathrm{K} + \sum_{i=1}^{i=n} k_b^{(i)} e_i} \qquad \ldots\ldots\ldots\ldots\ldots\ldots (12)$$

From (5) and (12) we have:

$$b^2 = \mathrm{K}. \frac{\mathrm{K} + \sum_{i=1}^{i=n} k_b^{(i)} e_i}{\mathrm{K} + \sum_{i=1}^{i=n} k_a^{(i)} e_i} \qquad \ldots\ldots\ldots\ldots\ldots\ldots (13)$$

From (6) and (12) we have:

$$c_n = \frac{k_a^{(n)} e_n}{\sqrt{\mathrm{K}}} \sqrt{\frac{\mathrm{K} + \sum_{i=1}^{i=n} k_b^{(i)} e_i}{\mathrm{K} + \sum_{i=1}^{i=n} k_a^{(i)} e_i}} \qquad \ldots\ldots\ldots\ldots\ldots\ldots (14)$$

From (7) and (13) we have:

$$d_n = \frac{k_b^{(n)} e_n}{\sqrt{\mathrm{K}}} \sqrt{\frac{\mathrm{K} + \sum_{i=1}^{i=n} k_a^{(i)} e_{(i)}}{\mathrm{K} + \sum_{i=1}^{i=n} k_b^{(i)} e_i}} \qquad \ldots\ldots\ldots\ldots\ldots\ldots (15)$$

From (6) and (7) by multiplication and substitution from (5) we obtain:

$$c_n d_m = \frac{k_b^{(n)} k_b^{(m)} e_n e_m}{\mathrm{K}}.$$

So that from (8) we see that

$$\sum_{i=1}^{i=n}\sum_{j=1}^{j=n} Q^{(i+j)} f_{i+j} = \frac{1}{K}\sum_{i=1}^{i=n}\sum_{j=1}^{j=n} k_a^{(i)} k_b^{(j)} e_i e_j \quad \ldots\ldots\ldots(16)$$

From (7)

$$d_n = \frac{1}{b} k_b^{(n)} e_n \ldots\ldots\ldots(17)$$

and from (6)

$$c_n = \frac{1}{a} k_a^{(n)} e_n \ldots\ldots\ldots(18)$$

$$\therefore \frac{d_n}{c_n} = \frac{a}{b} \cdot \frac{k_b^{(n)}}{k_a^{(n)}}$$

and from (5)

$$\frac{d_n}{c_n} = \frac{k_b^{(n)}}{K\, k_a^{(n)}} \cdot a^2$$

$$\therefore \sum_{i=1}^{i=n} \frac{d_i}{c_i} = \frac{a^2}{K} \sum_{i=1}^{i=n} \frac{k_b^{(i)}}{k_a^{(i)}} \ldots\ldots\ldots(19)$$

Hence, we see that *the sum of the ratios of the active masses of the dissociated basic ampholates to the active masses of the dissociated acid ampholates of corresponding orders varies as the square of the hydrion concentration.* Similarly, the sum of the ratios of the active masses of the dissociated acid ampholates to the active masses of the dissociated basic ampholates of corresponding orders varies as the square of the hydroxidion concentration.

Examining equation (12) we see that when $k_b^{(i)} = 0$ for all values of i, that is, when the basic function is zero and the substance is therefore a non-amphoteric acid we have:

$$a^2 = K + \sum_{i=1}^{i=n} k_a^{(i)} e_i \ldots\ldots\ldots(20)$$

which is a generalized form of Ostwald's dilution law, capable of application to *non-amphoteric acids which undergo associa-*

tion in solution. It is probably subject, however, to the same limitations as Ostwald's dilution-law, for we have throughout assumed that K, the ionic product for water, is constant; now it is possible that the addition of the ions of a strong electrolyte increases the dissociating power of water,[1] and in this case K, in equation (20) would no longer be constant. This limitation probably does not apply to equations (12–15), for ampholytes are usually weak electrolytes, since the presence of the basic function weakens the acid function and vice-versa. The same considerations hold good for the rest of the equations in this paper except where non-amphoteric electrolytes are involved, in which case, unless the non-amphoteric acids or bases are weak, K may not be constant.

If, in equation (12), $k_b^{(i)} = 0$ for all values of i while $k_a^{(i)} = 0$ for all values of i except $i = 1$, that is, if the electrolyte is non-associating and non-amphoteric, we have:

$$a^2 = K + k_a c \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (21)$$

which is simply Ostwald's dilution-law.[2]

If $k_a^{(i)} = k_b^{(i)}$ for all values of i, that is, if the acid and basic functions of all the ampholates are approximately equal, the equation (12) reduces to:

$$a = \sqrt{K}$$

that is, the concentration of hydrion and hydroxidion is equal to the concentration of these ions in pure water, that is, the substance is at all dilutions absolutely neutral, a condition of affairs which is probably approximately illustrated by a solution of egg-albumin in water;[3] a solution of such a substance resembles, in this respect, that of an ideal neutral salt, but differs from it in respect to the influence of dilution upon the dissociation.

From (17) and (18) we have:

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[1] Arrhenius: "Text-book of Electrochemistry," Trans. by J. McCrae, 1902, p. 165.

[2] Compare Walker: Proc. Roy. Soc., 73, 155 (1904).

[3] Vide Gustav Mann: "The Chemistry of the Proteids," (1906) p. 223.

$$\frac{c_n + d_n}{e} = \frac{1}{a} k_a^{(n)} + \frac{1}{b} k_b^{(n)}.$$

Hence, from (5),

$$\frac{c_n + d_n}{e_n} = \frac{1}{a} k_a^{(n)} + \frac{a}{K} k_b^{(n)}$$

$$\therefore \sum_{i=1}^{i=n} \frac{c_i + d_i}{e_i} = \frac{1}{Ka} \sum_{i=1}^{i=n} (K k_a^{(i)} + a^2 k_b^{(i)}) \ldots\ldots\ldots (22)$$

Now if $k_a^{(i)} = k_b^{(i)}$ we have shown that $a = \sqrt{K}$, and (22) becomes:

$$\sum_{i=1}^{i=n} \frac{c_i + d_i}{e_i} = \frac{2}{\sqrt{K}} \sum_{i=0}^{i=n} k_a^{(i)}.$$

That is, in an ampholyte, the acid and basic functions of which are equal, the sum of the ratios of dissociated to undissociated ampholytes of corresponding orders is independent of the dilution.

From equation (19) we see that when $k_a^{(i)} = k_b^{(i)}$ and $a = \sqrt{K}$, then $\sum_{i=1}^{i=n} d_i = \sum_{i=0}^{i=n} c_i$, that is, *in a solution of an ampholyte the acid and basic functions of which are equal, the active mass of the dissociated acid ampholates is equal to the active mass of the dissociated basic ampholates.*

B. The Conditions of Equilibrium of an Associating Ampholyte, the Ions of Which Are All Univalent, in the Presence of Any Number of Non-Amphoteric Electrolytes, the Ions of Which Are All Univalent

As in the case just considered, let the masses of the various substances for equilibrium be represented as follows:

H^+	OH'	XOH'	$XX....OH'$	HX^+	$HXX....X^+$
a	b	c_1	c_n	d_1	d_n

$HXOH$	$HXX....OH$	XX	$XX....X$	C_1^+	$C_{n'}^+$	A_1'
e_1	e_n	f_1	f_{2n}	β_1	$\beta_{n'}$	γ_1

$$\underset{\gamma_{n''}}{A'_{n''}} \quad \underset{\delta_{n'+m''}}{C_{n'}A_{m''}} \quad \underset{\eta_1}{C_1OH} \quad \underset{\eta_{n'}}{C_{n'}OH} \quad \underset{\theta_1}{A_1H} \quad \underset{\theta_{n''}}{A_{n''}H} \quad \underset{d'_{n'+m}}{C_{n'}XX\ldots.X^+}$$

$$\underset{C'_{m+n''}}{XX\ldots.A'_{n''}} \quad \underset{\lambda_{n'+m}}{C_{n'}XX\ldots.OH} \quad \underset{\mu_{m+n''}}{HXX\ldots.A_{n''}} \quad \underset{\pi_{l'+m+n''}}{C_{l'}XX\ldots.A_{n''}}$$

For equilibrium between the various positive and negative ions in pairs we have:

$$ab = K \qquad \ldots\ldots(23)$$

$$\left.\begin{aligned} ac_1 &= k_a^{(1)}e_1 \\ &\vdots\vdots \\ ac_n &= k_a^{(n)}e_n \end{aligned}\right\} \qquad \ldots\ldots(24)$$

$$\left.\begin{aligned} a\gamma_1 &= \rho_a^{(1)}\theta_1 \\ &\vdots\vdots \\ a\gamma_{n''} &= \rho_a^{(n'')}\theta_{n''} \end{aligned}\right\} \qquad \ldots\ldots(25)$$

$$ac'_{m+n''} = r_a^{(m+n'')}\mu_{m+n''} \qquad \ldots\ldots(26)$$

$$\left.\begin{aligned} bd_1 &= k_b^{(1)}e_1 \\ &\vdots\vdots \\ bd_n &= k_b^{(n)}e_n \end{aligned}\right\} \qquad \ldots\ldots(27)$$

[1] It will be observed that in this scheme of the substances in equilibrium we have distinguished between the subscripts n, n', and n'' denoting the number of variates in the classes represented by HXOH and its derivatives, C, or the cations which are *not H ions and their derivatives*, and A, or the anions which are not OH ions, and their derivatives. The reason for this is that while the number of variates in the classes, the masses of which are represented by the symbols d, c, and e, etc., must be identical, the number of variates in the classes β and γ are independent of each other and of the number of variates in the class ϵ. For example, although there may be n different ampholytes present in the system, the number of different cations present, derived from non-amphoteric electrolytes, *may* be arbitrarily chosen and probably bears no necessary relation to n, whereas the number of different ions derived from the ampholates obviously depends upon the number of different ampholates present. The necessity for this distinction did not arise in considering the system A, for there we had only one independent variable or class of independent variables, whereas in the present instance we have to deal with three classes of independent variables.

$$\left.\begin{aligned} b\beta_1 &= \rho_b^{(1)}\eta_1 \\ &\cdots\cdots \\ b\beta_{n'} &= \rho_b^{(n')}\eta_{n'} \end{aligned}\right\} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (28)$$

$$bd'_{n'+m} = \gamma^{(n'+m)}\lambda_{n'+m} \quad \ldots\ldots\ldots\ldots\ldots\ldots (29)$$

$$c_n d_m = Q_{n+m} f_{n+m} \quad \ldots\ldots\ldots\ldots\ldots\ldots (30)$$

$$c_n \beta_{m'} = R_{(n+m')}\lambda_{n+m'} \quad \ldots\ldots\ldots\ldots\ldots\ldots (31)$$

$$d_n \gamma_{m''} = S_{n+m''}\mu_{n+m''} \quad \ldots\ldots\ldots\ldots\ldots\ldots (32)$$

$$\beta_{n'}\gamma_{m''} = \Pi_{n'+m''}\delta_{n'+m''} \quad \ldots\ldots\ldots\ldots\ldots\ldots (33)$$

$$c_l d'_{n'+m} = \tau_{(l+m)+n'}\lambda_{(l+m)+n'} \quad \ldots\ldots\ldots\ldots\ldots\ldots (34)$$

$$d_l c'_{m+n''} = \tau'_{(l+m)+n''}\lambda_{(l+m)+n''} \quad \ldots\ldots\ldots\ldots\ldots\ldots (35)$$

$$d'_{l+m}\gamma_{n''} = G_{l+m+n'}\pi_{l+m+n''} \quad \ldots\ldots\ldots\ldots\ldots\ldots (36)$$

$$c'_{m+n''}\beta_l = G'_{l+m+n''}\pi_{l+m+n''} \quad \ldots\ldots\ldots\ldots\ldots\ldots (37)$$

$$d'_{l+m}c'_{n+o''} = Q'_{l+(m+n)+o''}\pi_{l+(m+n)+o''} \quad \ldots\ldots\ldots\ldots\ldots\ldots (38)$$

Equating the sums of the concentrations of the ions of opposite signs we have:

$$a + d_1 + \ldots + d_n + \beta_1 + \ldots + \beta_{n'} + d_1' + \ldots + d'_{n'+m} = b + c_1 + \ldots + c_n + \gamma_1 + \ldots + \gamma_{n'} + c_1' + \ldots + c'_{m+n''} \quad \ldots\ldots\ldots\ldots\ldots\ldots (39)$$

From (27) we have:

$$b(d_1 + \ldots + d_n) = k_b^{(1)}e_1 + \ldots + k_b^{(n)}e_n$$

$$\therefore \quad d_1 + \ldots + d_n = \frac{1}{b}\sum_{i=1}^{i=n} k_b^{(i)}e_i \quad \ldots\ldots\ldots\ldots\ldots\ldots (40)$$

Similarly:

$$\beta_1 + \ldots + \beta_{n'} = \frac{1}{b}\sum_{i=1}^{i=n'} \rho_b^{(i)}\eta_i \quad \ldots\ldots\ldots\ldots\ldots\ldots (41)$$

$$d_1' + \ldots + d'_{n'+m} = \frac{1}{b}\sum_{i=1}^{i=n'}\sum_{j=1}^{j=m} r_b^{(i+j)}\lambda_{i+j} \quad \ldots\ldots\ldots\ldots\ldots\ldots (42)$$

$$c_1 + \ldots + c_n = \frac{1}{a}\sum_{i=1}^{i=n} k_a^{(i)} e_i \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(43)$$

$$\gamma_1 + \ldots + \gamma_{n''} = \frac{1}{a}\sum_{i=1}^{i=n''} \rho_a^{(i)} \theta_i \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(44)$$

$$c_1' + \ldots + c'_{m+n''} = \frac{1}{a}\sum_{i=1}^{i=m}\sum_{j=1}^{j=n''} r_a^{(i+j)} \mu_{i+j} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(45)$$

Substituting from equations (40–45) in (39) we have:

$$a + \frac{1}{b}\sum_{i=1}^{i=n} k_b^{(i)} e_i + \frac{1}{b}\sum_{i=1}^{i=n'} \rho_b^{(i)} \eta_i + \frac{1}{b}\sum_{i=1}^{i=n'}\sum_{j=1}^{j=n} r_b^{(i+j)} \lambda_{i+j}$$

$$= b + \frac{1}{a}\sum_{i=1}^{i=n} k_a^{(i)} e_i + \frac{1}{a}\sum_{i=1}^{i=n''} \rho_a^{(i)} \theta_i + \frac{1}{a}\sum_{i=1}^{i=n}\sum_{j=1}^{j=n''} r_a^{(i+j)} \mu_{i+j}.$$

Multiplying both sides of this equation by a^2b we have:

$$a^2.ab + a^2\sum_{i=1}^{i=n} k_b^{(i)} e_i + a^2\sum_{i=1}^{i=n'} \rho_b^{(i)} \eta_i + a^2\sum_{i=1}^{i=n'}\sum_{j=1}^{j=n} r_b^{(i+j)} \lambda_{i+j} =$$

$$a^2b^2 + ab\sum_{i=1}^{i=n} k_a^{(i)} e_i + ab\sum_{i=1}^{i=n''} \rho_a^{(i)} \theta_i + ab\sum_{i=1}^{i=n}\sum_{j=1}^{j=n''} r_a^{(i+j)} \mu_{i+j}.$$

Hence from (23) we have:

$$a^2K + a^2\sum_{i=1}^{i=n} k_b^{(i)} e_i + a^2\sum_{i=1}^{i=n'} \rho_b^{(i)} \eta_i + a^2\sum_{i=1}^{i=n'}\sum_{j=1}^{j=n} r_b^{(i+j)} \lambda_{i+j}$$

$$= K^2 + K\sum_{i=1}^{i=n} k_a^{(i)} e_i + K\sum_{i=1}^{i=n''} \rho_a^{(i)} \theta_i + K\sum_{i=1}^{i=n}\sum_{j=1}^{j=n''} r_a^{(i+j)} \mu_{i+j}$$

$$\therefore\ a^2 = K\,\frac{K + \sum_{i=1}^{i=n} k_a^{(i)} e_i + \sum_{i=1}^{i=n''} \rho_a^{(i)} \theta_i + \sum_{i=1}^{i=n}\sum_{j=1}^{j=n''} r_a^{(i+j)} \mu_{i+j}}{K + \sum_{i=1}^{i=n} k_b^{(i)} e_i + \sum_{i=1}^{i=n'} \rho_b^{(i)} \eta_i + \sum_{i=1}^{i=n'}\sum_{j=1}^{j=n} r_b^{(i+j)} \lambda_{i+j}} \ldots(46)$$

Now from (32) we have:

$$\mu_{n+m''} = \frac{d_n \gamma_{m''}}{S_{n+m''}} \quad \ldots\ldots(47)$$

while from (27)

$$d_n = \frac{k_b^{(n)} e_n}{b} \quad \ldots\ldots(48)$$

and from (25)

$$\gamma_{m''} = \frac{\rho_a^{(m'')}\theta_{m''}}{a} \quad \ldots\ldots(49)$$

hence, substituting from (48), (49) and (23) in (47) we have:

$$\mu_{n+m''} = \frac{k_b^{(n)} \rho_a^{(m'')} e_n \theta_{m''}}{KS_{n+m''}}$$

$$\therefore \quad \gamma_a^{(n+m'')}\mu_{n+m''} = \frac{\gamma_a^{(n+m'')} k_b^{(n)} \rho_a^{(m'')} e_n \theta_{m''}}{KS_{n+m''}} \quad \ldots\ldots(50)$$

Similarly, from (31), (24) and (28) we obtain:

$$\gamma_b^{(n'+m)}\lambda_{n'+m} = \frac{\gamma_b^{(n'+m)} k_a^{(m)} \rho_b^{(n')} e_m \eta_{n'}}{KR_{n'+m}} \quad \ldots\ldots(51)$$

Substituting from (50) and (51) in (46) we have:

$$a^2 + K \frac{K + \sum_{t=1}^{t=n} k_a^{(t)} e_t + \sum_{t=1}^{t=n''} \rho_a^{(t)} \theta_t + \frac{1}{K} \sum_{i=1}^{t=n} \sum_{j=1}^{j=n''} \frac{\gamma_a^{(i+j)} k_b^{(i)} \rho_a^{(j)} e_i \theta_j}{S_{i+j}}}{K + \sum_{t=1}^{t=n} k_b^{(t)} e_t + \sum_{t=1}^{t=n'} \rho_b^{(t)} \eta_t + \frac{1}{K} \sum_{i=1}^{t=n'} \sum_{j=1}^{j=n} \frac{\gamma_b^{(i+j)} k_a^{(j)} \rho_b^{(i)} e_j \eta_i}{R_{i+j}}} \quad \ldots\ldots(52)$$

From (23) and (52) we have:

$$b^2 = K \frac{K + \sum_{t=1}^{t=n} k_b^{(t)} e_t + \sum_{t=1}^{t=n'} \rho_b^{(t)} \eta_t + \frac{1}{K} \sum_{i=1}^{t=n'} \sum_{j=1}^{j=n} \frac{\gamma_b^{(i+j)} k_a^{(j)} \rho_b^{(i)} e_j \eta_i}{R_{i+j}}}{K + \sum_{t=1}^{t=n} k_a^{(t)} e_t + \sum_{t=1}^{t=n''} \rho_a^{(t)} \theta_t + \frac{1}{K} \sum_{i=1}^{t=n} \sum_{j=1}^{j=n''} \frac{\gamma_a^{(i+j)} k_b^{(i)} \rho_a^{(j)} e_i \theta_j}{S_{i+j}}} \quad \ldots\ldots(53)$$

From (24) and (52) we have:

$$c_n = \frac{k_a^{(n)} e_n}{\sqrt{K}} \sqrt{\frac{K + \sum_{t=1}^{t=n} k_b^{(t)} e_t + \sum_{t=1}^{t=n'} \rho_b^{(t)} \eta_t + \frac{1}{K} \sum_{t=1}^{t=n'} \sum_{j=1}^{j=n} \frac{r_b^{(t+j)} k_a^{(j)} \rho_b^{(t)} e_j \eta_t}{R_{t+j}}}{K + \sum_{t=1}^{t=n} k_a^{(t)} e_t + \sum_{t=1}^{t=n''} \rho_a^{(t)} \theta_t + \frac{1}{K} \sum_{t=1}^{t=n} \sum_{j=1}^{j=n''} \frac{r_a^{(t+j)} k_b^{(t)} \rho_a^{(j)} e_t \theta_j}{S_{t+j}}}} \quad \ldots(54)$$

From (27) and (53) we have:

$$d_n = \frac{k_b^{(n)} e_n}{\sqrt{K}} \sqrt{\frac{K + \sum_{t=1}^{t=n} k_a^{(t)} e_t + \sum_{t=1}^{t=n''} \rho_a^{(t)} \theta_t + \frac{1}{K} \sum_{t=1}^{t=n} \sum_{j=1}^{j=n''} \frac{r_a^{(t+j)} k_b^{(t)} \rho_a^{(j)} e_t \theta_j}{S_{t+j}}}{K + \sum_{t=1}^{t=n} k_b^{(t)} e_t + \sum_{t=1}^{t=n'} \rho_b^{(t)} \eta_t + \frac{1}{K} \sum_{t=1}^{t=n'} \sum_{j=1}^{j=n} \frac{r_b^{(t+j)} k_a^{(j)} \rho_b^{(t)} e_j \eta_i}{R_{t+j}}}} \quad \ldots(55)$$

Similarly, $\gamma_{n''}$, $c'_{m+n''}$, $\beta_{n'}$ and $d'_{n'+m}$ can be found in terms of e_n, $\eta_{n'}$ and $\theta_{n''}$ and of the constants involved.

From (24) and (27), by multiplication and substitution from (23), we obtain:

$$c_n d_m = \frac{k_a^{(n)} k_b^{(m)} e_n e_m}{K}.$$

Hence, from (30):

$$\sum_{t=1}^{t=n} \sum_{j=1}^{j=n} Q_{t+j} f_{t+j} = \frac{1}{K} \sum_{t=1}^{t=n} \sum_{j=1}^{j=n} k_a^{(t)} k_b^{(j)} e_t e_j \quad \ldots\ldots\ldots(56)$$

From (33) $\delta_{n'+m''}$ can be found in terms of $\beta_{n'}$ and $\gamma_{m''}$ while from (38) $\pi_{t'+(m+n)+o''}$ can be found in terms of $d'_{t'+m}$ and $c'_{n+o''}$; now we have already seen that $\gamma_{n''}$, $c'_{m+n''}$, $\beta_{n'}$ and $d'_{n'+m}$ can be found in terms of e_n, $\eta_{n'}$, and $\theta_{n''}$, so that the active masses of all the variables in the system can be expressed in terms of the active masses of the undissociated ampholates, the active masses of the undissociated non-amphoteric acids, and the active masses of the undissociated non-amphoteric bases.

From (27)

$$d_n = \frac{k_b^{(n)} e_n}{b} \quad \ldots\ldots\ldots(57)$$

and from (24)

$$c_n = \frac{k_a^{(n)} e_n}{a} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (58)$$

$$\therefore \quad \frac{d_n}{c_n} = \frac{a}{b} \cdot \frac{k_b^{(n)}}{k_a^{(n)}}$$

and from (23)

$$\frac{d_n}{c_n} = \frac{k_b^{(n)}}{k_a^{(n)}} \cdot \frac{a^2}{K}$$

$$\therefore \quad \sum_{i=1}^{i=n} \frac{d_i}{c_i} = \frac{a^2}{K} \sum_{i=1}^{i=n} \frac{k_b^{(i)}}{k_a^{(i)}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (59)$$

Hence we see that, as in the case of System A, *the sum of the ratios of the active masses of the dissociated basic ampholates to the active masses of the acid ampholates varies as the square of the hydrion concentration.*

Similarly, the sum of the ratios of the active masses of the dissociated acid ampholates to the active masses of the dissociated basic ampholates varies as the square of the hydroxidion concentration.

From (25)

$$a = \frac{\rho_a^{(n'')} \theta_{n''}}{\gamma_{n''}} = \frac{\rho_a^{(m'')} \theta_{m''}}{\gamma_{m''}}$$

$$\therefore \quad a = \frac{\sum_{i=1}^{i=n''} \rho_a^{(i)} \theta_i}{\sum_{i=1}^{i=n''} \gamma_i}.$$

Hence, from (57),

$$\sum_{i=1}^{i=n} \frac{d_i}{c_i} = \frac{1}{K} \left(\frac{\sum_{i=1}^{i=n''} \rho_a^{(i)} \theta_i}{\sum_{i=1}^{i=n''} \gamma_i} \right)^2 \sum_{i=1}^{i=n} \frac{k_b^{(i)}}{k_a^{(i)}} \quad \ldots\ldots\ldots\ldots\ldots\ldots (60)$$

That is, *the sum of the ratios of the active masses of the dissociated basic ampholates to the active masses of the dissociated acid ampholates varies as the square of the ratio of the sum of the active masses of the undissociated non-amphoteric acids to the sum of the active masses of their dissociated parts.*

From (23) and (59)

$$\sum_{t=1}^{t=n}\frac{d_t}{c_t}=\frac{K}{b^2}\sum_{t=1}^{t=n}\frac{k_b^{(t)}}{k_a^{(t)}} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(61)$$

Now from (28)

$$b=\frac{\rho_b^{(n')}\eta_{n'}}{\beta_{n'}}=\frac{\rho_b^{(m')}\eta_{m'}}{\beta_{m'}}$$

$$\therefore\quad b=\frac{\sum_{t=1}^{t=n'}\rho_b^{(t)}\eta_t}{\sum_{t=1}^{t=n'}\beta_t}.$$

Hence, from (61),

$$\sum_{t=1}^{t=n}\frac{d_t}{c_t}=K\left(\frac{\sum_{t=1}^{t=n'}\beta_t}{\sum_{t=1}^{t=n'}\rho_b^{(t)}\eta_t}\right)^2\sum_{t=1}^{t=n}\frac{k_b^{(t)}}{k_a^{(t)}} \qquad \ldots\ldots\ldots\ldots\ldots\ldots(62)$$

That is, the sum of the ratios of the active masses of the dissociated basic ampholates to the active masses of the dissociated acid ampholates also varies as the square of the ratio of the sum of the active masses of the *dissociated* non-amphoteric bases to the sum of the active masses of their *undissociated* parts.

From (24) we have:

$$\frac{c_n}{e_n}=\frac{k_a^{(n)}}{a}$$

and from (27) we have:

$$\frac{d_n}{e_n} = \frac{k_b^{(n)}}{b}$$

$$\therefore \frac{d_n + c_n}{e_n} = k_a^{(n)} \cdot \frac{1}{a} + \frac{k_b^{(n)}}{K} \cdot a \text{ (from 23)}$$

$$\therefore \sum_{i=1}^{i=n} \frac{d_i + c_i}{e_i} = \frac{1}{Ka}\left(K \sum_{i=1}^{i=n} k_a^{(i)} + a^2 \sum_{i=1}^{i=n} k_b^{(i)} \right) \ldots\ldots\ldots (63)$$

By substituting from (23) and rearranging, this equation may also be written:

$$\sum_{i=1}^{i=n} \frac{d_i + c_i}{e_i} = \frac{1}{Kb}\left(b^2 \sum_{i=1}^{i=n} k_a^{(i)} + K \sum_{i=1}^{i=n} k_b^{(i)} \right) \ldots\ldots\ldots (64)$$

Now $\sum_{i=1}^{i=n} \frac{d_i + c_i}{e_i}$ is the sum of the ratios of the dissociated ampholates to the undissociated ampholates, and from (63) we see that when a is small $\sum_{i=1}^{i=n} \frac{d_i + c_i}{e_i}$ varies inversely as a, that is, from (23), directly as b and, similarly, when b is small $\sum_{i=1}^{i=n} \frac{d_i + c_i}{e_i}$ varies directly as a. Hence, when the hydrion concentration is small the dissociation of the ampholates varies directly as the hydroxidion concentration, while, when the hydroxidion concentration is small the dissociation of the ampholates varies directly as the hydrion concentration. Differentiating the right-hand side of equation (63) with respect to a and equating to zero, since the second derivative is positive for all positive values of a, we find that $\sum_{i=1}^{i=n} \frac{d_i + c_i}{e_i}$ is at a minimum when $a^2 = K \frac{\sum_{i=1}^{i=n} k_a^{(i)}}{\sum_{i=1}^{i=n} k_b^{(i)}}$ and $b^2 = K \cdot \frac{\sum_{i=1}^{i=n} k_b^{(i)}}{\sum_{i=1}^{i=n} k_a^{(i)}}$, and substi-

tuting in (59) we see that *at this hydrion concentration the sum of the active masses of the dissociated acid ampholates is equal to the sum of the active masses of the dissociated basic ampholates.*

From equation (56) we see that *when the dissociation of the ampholates is at a minimum the association is at a maximum,*

hence the association is at a maximum when $a^2 = K \frac{\sum_{i=1}^{i=n} k_a^{(i)}}{\sum_{i=1}^{i=n} k_b^{(i)}}$.

There will, however, not only be a minimum value for the dissociation of all the ampholates present, taken together, but also for the dissociation of each ampholate in the system and for the dissociation of any given group of the ampholates. Thus the minimum value of the dissociation of the ampholates of orders 1 to m will be given by $a^2 = \frac{\sum_{i=1}^{i=m} k_a^{(i)}}{\sum_{i=1}^{i=m} k_b^{(i)}}$ and this value for a will not necessarily be the same as that given by $a^2 = \frac{\sum_{i=1}^{i=n} k_a^{(i)}}{\sum_{i=1}^{i=n} k_b^{(i)}}$. Hence, if n different ampholates be present the total number of minima of dissociation of one or more of the ampholates will be equal to "the total number of combinations" of n things, that is, to $2^n - 1$. The condition that all these minima should coincide is $\frac{k_a^{(m)}}{k_b^{(m)}} = \frac{k_a^{(n)}}{k_b^{(n)}}$ where m and n have any values, that is, that the ratio of the acid function to the basic function must be the same for all the ampholates, a condition that not impossibly holds good in protein systems. In any case the value of a at the minimum value for the

dissociation of *all* the ampholates of orders 1 to n will lie *between* the upper and lower values of a given by the minimum values for the dissociation of all the possible combinations of $n - m$ ampholates[1] where n and m have any values and the ampholates are of the orders 1 to n.

Since association increases as dissociation decreases these minima of dissociation not improbably represent minima of solubility, provided that the larger molecule-complexes are less soluble than the smaller complexes.

From equations (31) and (32) we see that the individual *salts* of the ampholates show no true minima of dissociation but that their dissociation diminishes continuously with the increase in concentration of the corresponding non-amphoteric ion. Upon this depends the "salting out" of proteins, using the term "salting out" in the sense in which it is used in speaking of the salting out of soaps.

Ions of the amphoteric system may be derived, however, not only from ampholates of the type HXX....OH, from their salts dissociating as such and from their association-salts, but also from ampho-salts of the types $C_{n'}XX....OH$ and $HXX...A_{n''}$ acting as bases and as acids respectively and from their di-salts.

The ions thus derived will contain undissociated non-amphoteric cations or anions other than hydrogen and hydroxyl ions and upon the formation of such ions and of the molecules derived therefrom probably depends the existence in tissues of undissociated metal and other ions to which Loeb has drawn attention.[2]

From (26) we see that:

$$\frac{c'_{m+n''}}{\mu_{m+n'}} = \gamma_a^{(m+n')} \cdot \frac{1}{a}$$

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[1] For if $\frac{a}{b}, \frac{c}{d} \ldots$ etc., be unequal fractions and if $x = z(a + c + \ldots)$ and $y = z(b + d + \ldots)$ then the fraction $\frac{x}{y}$ lies in value between the greatest and least of the fractions $\frac{a}{b}, \frac{c}{d} \ldots$. etc.

[2] J. Loeb: "Dynamics of Living Matter," Columbia Univ. Press, 1906, p. 72.

and from (29) and (23) we have:

$$\frac{d'_{n'+l}}{\lambda_{n'+l}} = \gamma_b^{(n'+l)} \cdot \frac{a}{K}.$$

Hence

$$\sum_{i=1}^{i=n}\sum_{j=1}^{j=n''}\frac{c'_{i+j}}{\mu_{i+j}} + \sum_{i=1}^{i=n'}\sum_{j=1}^{j=n}\frac{d'_{i+j}}{\lambda_{i+j}} = \frac{1}{Ka}\left(K\sum_{i=1}^{i=n}\sum_{j=1}^{j=n''}\gamma_a^{(i+j)} + a^2\sum_{i=1}^{i=n'}\sum_{j=1}^{j=n}\gamma_b^{(i+j)}\right) \quad \ldots\ldots\ldots(65)$$

By substituting from (23) and rearranging, this equation may also be written:

$$\sum_{i=1}^{i=n}\sum_{j=1}^{j=n''}\frac{c'_{i+j}}{\mu_{i+j}} + \sum_{i=1}^{i=n'}\sum_{j=1}^{j=n}\frac{d'_{i+j}}{\lambda_{i+j}} = \frac{1}{Kb}\left(b^2\sum_{i=1}^{i=n}\sum_{j=1}^{j=n''}\gamma_a^{(i+j)} + K\sum_{i=1}^{i=n'}\sum_{j=1}^{j=n}\gamma_b^{(i+j)}\right) \quad \ldots\ldots\ldots(66)$$

Now the left-hand side of equations (65) and (66) is the sum of the ratios of the masses of the dissociated acid and basic ampho-salts to the masses of the undissociated ampho-salts, and from (65) we see that when a is small $\sum_{i=1}^{i=n}\sum_{j=1}^{j=n''}\frac{c'_{i+j}}{\mu_{i+j}} + \sum_{i=1}^{i=n'}\sum_{j=1}^{j=n}\frac{d'_{i+j}}{\lambda_{i+j}}$ varies inversely as a, that is, from (23), directly as b, and, similarly, when b is small $\sum_{i=1}^{i=n}\sum_{j=1}^{j=n''}\frac{c'_{i+j}}{\mu_{i+j}} + \sum_{i=1}^{i=n'}\sum_{j=1}^{j=n}\frac{d'_{i+j}}{\lambda_{i+j}}$ varies directly as a. Hence the acid and basic ampho-salts, taken together, behave, as regards the influence of the hydrion and hydroxidion concentration upon their dissociation, analogously to the acid and basic ampholates. Equation (65) may be written:

$$\sum_{i=1}^{i=n}\sum_{j=1}^{j=n'}\frac{c'_{i+j}}{\mu_{i+j}}+\sum_{i=1}^{i=n'}\sum_{j=1}^{j=n}\frac{d'_{i+j}}{\lambda_{i+j}}=\frac{b}{K}\sum_{i=1}^{i=n}\sum_{j=1}^{j=n''}r_a^{(i+j)}+\frac{a}{K}\sum_{i=1}^{i=n'}\sum_{j=1}^{j=n}r_b^{(i+j)}\quad\ldots\ldots\ldots\ldots(67)$$

From (25)

$$a=\frac{\sum_{i=1}^{i=n''}\rho_a^{(i)}\theta_i}{\sum_{i=1}^{i=n''}\gamma_i},$$

and from (28)

$$b=\frac{\sum_{i=1}^{i=n'}\rho_b^{(i)}\eta_i}{\sum_{i=1}^{i=n'}\beta_i}.$$

Substituting in (67)

$$\sum_{i=1}^{i=n}\sum_{j=1}^{j=n''}\frac{c'_{i+j}}{\mu_{i+j}}+\sum_{i=1}^{i=n'}\sum_{j=1}^{j=n}\frac{d'_{i+j}}{\lambda_{i+j}}=\frac{1}{K}\left(\frac{\sum_{i=1}^{i=n'}\rho_b^{(i)}\eta_i}{\sum_{i=1}^{i=n'}\beta_i}\sum_{i=1}^{i=n}\sum_{j=1}^{j=n''}r_a^{(i+j)}+\frac{\sum_{i=1}^{i=n''}\rho_a^{(i)}\theta_i}{\sum_{i=1}^{i=n''}\gamma_i}\sum_{i=1}^{i=n'}\sum_{j=1}^{j=n}r_b^{(i+j)}\right)\ldots.(68)$$

Thus, if the solubility of the ampho-salts be considered as proportional to the sum of the ratios of the ionized to un-ionized material, it follows that in this system the solvent power of different salts is additive.

Differentiating the right-hand side of equation (65) with respect to a and equating to zero, since the second derivative

must be positive, we find that $\sum_{i=1}^{i=n}\sum_{j=1}^{j=n'}\frac{c'_{i+j}}{\mu_{i+j}}+\sum_{i=1}^{i=n'}\sum_{j=1}^{j=n}\frac{d_{i+j}}{\lambda_{i+j}}$ is a minimum when $a^2=K.\frac{\sum_{i=1}^{i=n}\sum_{j=1}^{j=n''}r_a^{(i+j)}}{\sum_{i=1}^{i=n'}\sum_{j=1}^{j=n}r_b^{(i+j)}}$ and $b^2=K.\frac{\sum_{i=1}^{i=n'}\sum_{j=1}^{j=n}r_b^{(i+j)}}{\sum_{i=1}^{i=n}\sum_{j=1}^{j=n''}r_a^{(i+j)}}$.

From equations (26) and (29) we see that in the case of the acid and basic ampho-salts *the sum of the active masses of the dissociated acid ampho-salts is not necessarily equal to the sum of the active masses of the dissociated basic ampho-salts when their dissociation is at a minimum.*

From (26)

$$c'_{n+o''}=\frac{r_a^{(n+o'')}\mu_{n+o''}}{a}.$$

Hence, from (23) and (29),

$$\sum_{i=1}^{i=n'}\sum_{j=1}^{j=n}\sum_{k=1}^{k=n}\sum_{l=1}^{l=n''}d_{i+j}c'_{k+l}=\sum_{i=1}^{i=n'}\sum_{j=1}^{j=n}\sum_{k=1}^{k=n}\sum_{l=1}^{l=n''}\frac{r_b^{(i+j)}.r_a^{(k+l)}\lambda_{i+j}\mu_{k+l}}{K} \quad (69)$$

Thus we see that, analogously to the ampholates, the association, or formation of di-salts of the acid and basic ampho-salts is at a maximum when their dissociation is at a minimum, that is, when $a^2=K\frac{\sum_{i=1}^{i=n}\sum_{j=1}^{j=n''}r_a^{(i+j)}}{\sum_{i=1}^{i=n'}\sum_{j=1}^{j=n}r_b^{(i+j)}}$. Just as in the case of the ampholates there will not only be a minimum value for the dissociation of all the acid or basic ampho-salts but also for the dissociation of each pair of acid and basic ampho-salts and for the dissociation of any given group of such ampho-salts. If n orders of ampholates, n' non-amphoteric cations and n'' non-amphoteric anions be present, the total number of acid ampho-salts will be nn'' and

the total number of basic ampho-salts will be nn' so that the total number of pairs of acid and basic ampho-salts will be $n^2n'n''$ and the total number of minima of dissociation of one or more of these pairs of ampho-salts will be equal to "the total number of combinations" of $n^2n'n''$ things, that is, to $2^{n^2n'n''}-1$. The condition that all these minima may coincide is $\frac{r_a^{(n+n'')}}{r_b^{(n'+1)}}$ =constant, which is obviously improbable.

Thus adding the number of possible minima of dissociation of the ampholates, the total number of possible minima of dissociation in the system under consideration is $2^{n^2n'n''}+2^n-2$, any of which may coincide.

It will be seen that the number of different minima of dissociation increases very rapidly with the number of different non-amphoteric ions present. Thus, if the ampholyte is non-associating, *i. e.*, $n=1$, the possible number of different minima of dissociation when two different non-amphoteric cations and one non-amphoteric anion are present is 4, but when two non-amphoteric cations and two non-amphoteric anions are present the possible number of minima becomes 16. As we shall see later, the number of minima of dissociation of the ampho-salts increases still more rapidly with the *valency* of the non-amphoteric ions.

In the case of proteins these minima do not necessarily imply the formation of precipitates, but they not improbably represent minima of solubility. The minima will be most marked, however, when the greatest number of the different substances present take part in its formation; that is, there will be two "chief" minima, indicated by equations (63) and (65) and $2^{n^2n'n''}+2^n-4$ "subsidiary" minima superimposed upon the chief minima. If, however, the ratio of the acid to the basic function be equal for all the ampholates in the system there will only be $2^{n^2n'n''}-4$ subsidiary minima. If no anions other than hydroxidion be present then n'' will be zero and there will obviously be no minima of dissociation due to acid and basic ampho-salts and there will only be one "chief"

minimum. Similarly, if no cations other than hydrions be present n' will be zero and there will again only be one "chief" minimum. We may here briefly indicate the possible bearing of these conclusions upon the phenomena of solubility, etc., in protein systems.

The researches of Spiro[1] and of Wolfgang Ostwald[2] appear to indicate a parallelism between the "swelling" of colloids and their solution. In fact, if swelling consists, as appears probable, in the increase of the water-rich, colloid-poor phase at the expense of the colloid-rich, water-poor phase,[3] then the two processes, swelling and solution, are probably fundamentally identical. The apparent difference consisting in the fact that in a solution of a colloid the water-rich phase is the "external phase" and the water-poor phase is the "internal phase,"[4] while in the swelling of colloids the water-rich phase is usually the internal phase and the water-poor phase external. Considering, therefore, the degree of swelling of a colloid in a given solution to run parallel with its solubility in that solution, the two large minima in the curve representing the degree of swelling of gelatine plates in different concentrations of salts, found by Wolfgang Ostwald,[5] probably represent the two "chief" minima of dissociation which our theoretical investigation has shown may exist in such a system, while the irregular character of the curves of swelling in different concentrations of various salts is probably to be attributed to the "subsidiary" minima of dissociation which, as we have seen, would be superimposed upon the "chief" minima in such a system. The formation of "pseudo-ions"[6] or associa-

[1] Spiro: Hofmeister's Beitr: Z. chem. Physiol., 5, 276 (1904).

[2] Wo. Ostwald: Pflüger's Arch. f. d. ges. Physiol., 108, 263 (1905); Ibid., 109, 277 (1905). Ibid., 111, 581 (1906).

[3] See W. B. Hardy: Proc. Roy. Soc., 66, 95 (1900); Jour. Phys. Chem., 4, 235, 254 (1900); Journal of Physiology, 33, 251 (1905); Spiro: Hofmeister's Beitr. zu. Chem. Physiol., 4, 300 (1903); Quincke: Drude's Ann., 10, 478, 673 (1903).

[4] W. B. Hardy has used and defined these terms in the papers to which I have just referred.

[5] Wo. Ostwald: Pflüger's Arch. f. d. ges. Physiol., 111, 581 (1906).

[6] W. B. Hardy: Jour. of Physiol., 33, 257 (1905).

tion salts in a protein solution would probably be accompanied by an increase in viscosity,[1] the complex ions acquiring the properties of matter in mass. Moreover, Hardy has observed in the paper to which I have just referred, that the opalescence of a globulin solution runs parallel with its viscosity, and this opalescence can only, I think, be attributed to the formation of large association-complexes. Now minima of dissociation in an ampholyte system correspond, as we have seen, to maxima of association and thus, according to the above reasoning, to maxima of viscosity. Hence, if our argument be correct, we should expect maxima of viscosity in solutions containing the same concentration of protein to correspond with minima of swelling of the same protein in the same solution. Here we have a possible explanation of the parallel found by Wolfgang Ostwald between the swelling of gelatine in salt solutions as determined by him[2] and the viscosity of such salt solutions containing equal concentrations of gelatine, as determined by von Schroeder.[3]

The fact that, as we have seen, when no non-amphoteric anions other than hydroxidions or when no non-amphoteric cations other than hydrions are present there is only one "chief" minimum of dissociation affords a possible explanation of the fact that Wolfgang Ostwald found only one distinct minimum of swelling of gelatine in different concentrations of acids or alkalies alone, while the relatively smooth character of these curves as contrasted with those obtained when swelling took place in salt solutions may possibly find an explanation in the equality of the ratios of the acid and basic functions of the ampholates of different orders which not improbably occurs in protein systems, for under these conditions there would theoretically be only one "chief" minimum and no "subsidiary" minima of dissociation. The general character of the curves of swelling in different concentrations of salts,

[1] W. B. Hardy : l. c., p. 285.
[2] Wo. Ostwald: Arch. f. d. ges. Physiol., 111, 581 (1906).
[3] Von Schroeder : Zeit. phys. Chem., 45, 75 (1903).

consisting, as they do, of a number of minor minima and maxima superimposed upon one or two large minima and maxima is in good agreement with the above argument.

The double minimum of solubility of protein in solutions of different concentrations of salts of the heavy metals, found by Pauli,[1] may also be alluded to in this connection.

From the above considerations it will be obvious that, provided the heavier, more complex molecules are less soluble than the lighter, simpler molecules, an ampholyte may be thrown out of solution in any one of three ways (chemically speaking).

(1) By approaching the "chief" minimum of dissociation of the ampholates.

(2) By the "salting out" of the ampho-salts which are dissociating as such.

(3) By approaching the "chief" minimum of dissociation of the acid and basic ampho-salts.

Now, at the "chief" minimum of dissociation of the ampholates, we have seen that the sum of the active masses of the dissociated acid ampholates is equal to the sum of the active masses of the dissociated basic ampholates. Now if, as Loeb and Hardy have suggested,[2] and as certainly appears probable, the charge on a colloid particle is due to its acid or alkaline nature, the "chief" minimum of dissociation of the ampholates will therefore correspond to the "iso-electric point" at which, as has been very well established by the researches of Hardy,[3] Perrin,[4] Billitzer,[5] Pauli[6] and others, precipitation very generally takes place. To attempt, however, as some have

[1] W. Pauli: Hofmeister's Beitr., 6, 233 (1905).

[2] J. Loeb: Univ of Calif. Pub., 1, 149 (1904); W. B. Hardy: Jour. Physiol., 33, 257 (1905); See also Picton and Linder: Jour. Chem. Soc., 71, 568 (1897).

[3] W. B. Hardy: Jour. Physiol., 24, 288 (1898); Proc. Physiol. Soc., May 16, 1903; Jour. Physiol., 29, (1903).

[4] Perrin: Jour. Chim. Phys., 2, 61 (1904); 3, 50 (1905).

[5] Billitzer: Drude's Ann., 2, 902 (1903); Zeit. phys. Chem., 45, 307 (1903); 51, 129 (1905).

[6] Pauli: Beitr. Exp. Physiol. u. Pathol., 3, 225 (1901); 5, 27 (1903); 6, 233 (1905).

done, to bring all classes of protein precipitation by electrolytes under this head is to ignore the other two possibilities of precipitation, owing to alterations in the chemical equilibrium of the system, namely, the "salting out" of the ampho-salts and the approaching of the "chief" minimum of dissociation of the acid and basic ampho-salts, at which, as has been pointed out, the active masses of the acid and basic ampho-salts or ampholates are not necessarily equal—the precise relation between them varying according to the nature of the electrolytes present and of the protein. Hence many exceptions to the rule of precipitation at the iso-electric point have been found.[1]

Examining equation (52) we see that it is no longer sufficient, in the system at present under consideration, that $k_a^{(n)} = k_b^{(n)}$ for all values of n in order that the reaction may be independent of the dilution, as it was in system A. In this system a variety of other conditions have to be fulfilled.

C. The Conditions of Equilibrium of Two Associating Ampholytes, the Ions of Which Are All Univalent, in the Presence of any Number of Non-Amphoteric Electrolytes, the Ions of Which Are All Univalent

As in the previous cases let the masses of the various substances for equilibrium be represented as follows:

H^+	OH'	XOH'	$XX....OH'$	HX^+	$HX....X^+$	$HXOH$		
a	b	c_1	c_n	d_1	d_n	e_1		
$HXX....OH$	XX	$XX...X$	ROH'	$RR....OH'$	HR^+			
e_n	f_2	f_{2n}	c_1''	$c''_{n'''}$	d_1''			
$HR....R^+$	$HROH$	$HRR....OH$	RR	$RR....R$				
$d''_{n'''}$								
$HX....R....OH$	$X....R....OH'$	$HX....R^+$	$XX....RR$					
C_1^+	$C^+_{n'}$	A_1'	$A'_{n''}$	$C_{n'}A_{m''}$	C_1OH	$C_{n'}OH$	A_1H	$A_{n''}H$
β_1	$\beta_{n'}$	γ_1	$\gamma_{n''}$	$\delta_{n'+m''}$	η_1	$\eta_{n'}$	θ_1	$\theta_{n''}$
$C_{n'}XXX^+$	$XX..A'_{n''}$	$C_{n'}RRR^+$	$RR...A'_{n''}$	$C_{n'}RR...XX^+$				
$d''_{n'+m}$	$C'_{m+n''}$							

[1] See particularly W. B. Hardy: Jour. Physiol., 33, 251 (1905).

$$XX\ldots RRA'_{n''} \quad C_{n'}XX\ldots OH \quad C_{n'}X\ldots R\ldots OH$$

$$\lambda_{n'+m}$$

$$HXX\ldots A_{n''} \quad HXX\ldots RRA_{n''}$$

$$\mu_{m+n''}$$

$$C_{l'}XX\ldots A_{n''} \quad c_{l'}XX\ldots RRA_{n''}{}^{1}$$

$$\pi_{l'+m+n''}$$

We will confine our investigations, in this system, to the interactions between the two ampholytes, with the production of substances of the type XX . . . . RR, so that only those equilibrium equations need be discussed which bear on this question. . . We have, at equilibrium:

$$ab = K \qquad \ldots\ldots(70)$$

$$\left.\begin{aligned} ac_1 &= k_a^{(1)} e_1 \\ &\vdots\ \vdots\ \vdots \\ ac_n &= k_a^{(n)} e_n \end{aligned}\right\} \qquad \ldots\ldots(71)$$

$$\left.\begin{aligned} ac''_1 &= p_a^{(1)} e'_1 \\ &\vdots\ \vdots\ \vdots \\ ac''_{n'''} &= p_a^{(n''')} e'_{n'''} \end{aligned}\right\} \qquad \ldots\ldots(72)$$

$$\left.\begin{aligned} bd_1 &= k_b^{(1)} e_1 \\ &\vdots\ \vdots\ \vdots \\ bd_n &= k_b^{(n)} e_n \end{aligned}\right\} \qquad \ldots\ldots(73)$$

$$\left.\begin{aligned} bd''_1 &= p_b^{(1)} e'_1 \\ &\vdots\ \vdots\ \vdots \\ bd''_{n'''} &= p_b^{(n''')} e'_{n'''} \end{aligned}\right\} \qquad \ldots\ldots(74)$$

From (73) and (71) we have:

$$d_n = \frac{k_b^{(n)} e_n}{b}$$

[1] In the above scheme only those active masses are denoted by symbols which have previously been so denoted or which will be required in the following investigation.

and

$$c_n = \frac{k_a^{(n)} e_n}{a}$$

and from (70)

$$\frac{d_n}{c_n} = \frac{a^2}{K} \cdot \frac{k_b^{(n)}}{k_a^{(n)}} \quad \ldots\ldots(75)$$

Similarly,

$$\frac{d''_{n'''}}{c''_{n'''}} = \frac{a^2}{K} \cdot \frac{p_b^{(n''')}}{p_a^{(n''')}} \quad \ldots\ldots(76)$$

Now the "active mass" of a protein ampholyte of the type HXX′... OH, as ordinarily measured, is probably $\sum_{i=1}^{i=n} c_i + \sum_{i=1}^{i=n} d_i$, while the measured active mass of the ampholyte of type HRR.... OH is $\sum_{i=1}^{i=n'''} c''_i + \sum_{i=1}^{i=n'''} d''_i$. But the reaction between the two ampholytes obviously takes place between the positive and negative ions in pairs, so that the condition that the measured active mass of the products of the reaction shall be proportional to the product of the *measured* active masses of the reacting substances is obviously that $\left(\sum_{i=1}^{i=n} c_i + \sum_{i=1}^{i=n} d_i\right)\left(\sum_{j=1}^{j=n'''} c''_j + \sum_{j=1}^{j=n'''} d''_j\right)$, which is the product of the *measured* active masses of the reacting substances, shall bear a constant proportion to $\sum_{i=1}^{i=n}\sum_{j=1}^{j=n'''} c_i d''_j + \sum_{i=1}^{i=n}\sum_{j=1}^{j=n'''} d_i c''_j$, which is the sum of the products of the active masses of the actually reacting ions.

That is, we have the following condition in order that Guldberg and Waage's mass law may be directly applied to such reactions as we are considering, namely, that

$\sum_{i=1}^{i=n}\sum_{j=1}^{j=n'''} c_i c''_j + \sum_{i=1}^{i=n}\sum_{j=1}^{j=n'''} d_i c''_j + \sum_{i=1}^{i=n}\sum_{j=1}^{j=n'''} c_i d''_j + \sum_{i=1}^{i=n}\sum_{j=1}^{j=n'''} d_i d''_j$ must be proportional to $\sum_{i=1}^{i=n}\sum_{j=1}^{j=n'''} c_i d''_j + \sum_{i=1}^{i=n}\sum_{j=1}^{j=n'''} d_i c''_j$.

From (75) we have

$$c_n c''_{m'''} = \frac{k_a^{(n)}}{k_b^{(n)}} \cdot \frac{K}{a^2} d_n c''_{m'''} \quad \ldots\ldots\ldots\ldots\ldots\ldots (77)$$

and

$$d_n d''_{m'''} = \frac{k_b^{(n)}}{k_a^{(n)}} \cdot \frac{a^2}{K} c_n d''_{m'''} \quad \ldots\ldots\ldots\ldots\ldots\ldots (78)$$

Hence:

$$c_n c''_{m'''} + d_n c''_{m'''} + c_n d''_{m'''} + d_n d''_{m'''} = \left(1 + \frac{k_a^{(n)}}{k_b^{(n)}} \cdot \frac{K}{a^2}\right) d_n c''_{m'''} + \left(1 + \frac{k_b^{(n)}}{k_a^{(n)}} \cdot \frac{a^2}{K}\right) c_n d''_{m'''}$$

The condition that the right-hand side of this equation may bear a constant proportion to $d_n c''_{m'''} + c_n d''_{m'''}$ is $a^2 = K.\frac{k_a^{(n)}}{k_b^{(n)}}$, that is, in order that Guldberg and Waage's mass law may be directly applied to the reaction between two different associating ampholytes *the hydrion concentration must be constant and equal to the square root of K multiplied by the square root of the ratio of the acid function to the basic function of one of the reacting ampholytes, and this ratio must be identical for each of the association salts formed from that ampholyte.* In other words, as will be evident from equation (59) and from the considerations on p. 555, *one of the reacting ampholytes must be iso-electric and must remain so throughout the reaction.* Since the above argument holds equally well for either ampholyte the mass law in its directly applicable form will obviously hold good whichever ampholyte is iso-electric, the condition in the case of the ampholyte of type HRR . . . . OH being $a^2 = K.\frac{k_a^{(n)}}{k_b^{(n)}}$.

Obviously, the mass law will also be directly applicable if in one of the reacting ampholytes the basic function far outweighs the acid function, so that the latter is negligible, while in the other the acid function far outweighs the basic function, for in that case both the equation obtained by measurement and the actual equilibrium equation reduce to $\sum_{i=1}^{i=n}\sum_{j=1}^{j=n'''} d_i c_j'' = \text{constant} \times \text{products}$, or to $\sum_{i=1}^{i=n}\sum_{j=1}^{j=n'''} c_i d_j'' = \text{constant} \times \text{products}$. It may possibly be found that these restrictions under which the mass law can be applied directly to two reacting ampholytes offer an explanation both of the successes and of the failures to apply the mass law directly to protein hydrolysis by enzymes and to the toxin, antitoxin and allied reactions, to which I have referred in the introduction.

D. The Conditions of Equilibrium of an Associating Ampholyte, the Ions of Which Are Partly Divalent and Partly Univalent, in the Presence of Any Number of Non-Amphoteric Electrolytes, the Ions of Which Are All Univalent

In respect to valency the proteins appear to fall into two classes. The one, to which, for example, serum globulin belongs[1] and which we may designate Class I, forms *molecular* compounds with acids and bases, combining by addition with either mono or dibasic acids, or with either mon or diacid bases. Such bodies naturally behave, so far as our purposes are concerned, as if the different ampholyte ions and non-amphoteric ions were of the same valency, so that the equations which hold good for systems A, B, and C will hold good as regards Class I, whether the ampholytes or non-amphoteric electrolytes are monacid and monobasic or diacid and dibasic, always remembering, however, that when plurivalent ions are present a much greater number and variety of ions are possible, owing to the formation of complex ions of lower valency by union of an ion of higher valency with ions of opposite sign

[1] W. B. Hardy : Jour. Physiol., 33, 251 (1905).

and lower valency—all of which must be included in the classes of ions, the masses of which are, in system B, represented by the symbols c_n d_m, c'_n, d_n,β'_n and γ''_n. 'The other class, Class II, to which casein belongs[1] combines with acids and bases in *equivalent* molecular proportions, so that here the equations found for system B do not apply if the system contains other than monovalent ions.

As in the cases previously considered, let the masses of the various substances for equilibrium be represented as follows:

H^+ OH' $X(OH)_2''$ $XX....(OH)_2''$ $HX(OH)_2'$ $HXX....(OH)_2'$
a b c_1 c_n c'''_1 c'''_n

H_2X^{++} $H_2X....X^{++}$ H_2XOH^+ $H_2X....XOH^+$ $H_2X(OH)_2$
d_1 d_n d'''_1 d'''_n e_1

$H_2X....X(OH)_2$ $XX....X$ C_1^+ $C_{n'}^+$ A'_1 $A'_{n''}$ $C_{n'}A_{m''}$
e_n f_{3n}[2] β_1 $\beta_{n'}$ γ_1 $\gamma_{n''}$ $\delta_{n'+m''}$

C_1OH $C_{n'}OH$ A_1H $A_{n''}H$ $(C_{n'})_2X...X^{++}$ $C_{n'}HX...X^{++}$
η_1 $\eta_{n'}$ θ_1 $\theta_{n''}$ $d'_{n'+m}$ $d'_{n'+m}$

$(C_{n'})_2XX...OH^+$ $C_{n'}HXX...OH^+$ $XX...(A_{n''})_2''$
$g_{n'+m}$ $g'_{n'+m}$ $c'_{m+n''}$

$XX...OHA''_{m''}$ $HXX...(A_{n''})'_2$ $HXX...OHA'_{n''}$
$c''_{m+n''}$ $h_{m+n''}$ $h'_{m+n''}$

$(C_{n'})_2XX...(OH)_2$ $C_{n'}HXX...(OH)_2$ $H_2XX...(A_{n''})_2$
$\lambda_{n'+m}$ $\lambda'_{n'+m}$ $\mu_{m+n''}$

$H_2XX...OHA_{n''}$ $(C_{l'})_2XX...(A_{n''})_2$ $C_{l'}HXX...(A_{n''})_2$
$\mu'_{m+n''}$ $\pi_{l'+m+n''}$ $\pi'_{l'+m+n''}$

$(C_{l'})_2XX...OHA_{n''}$ $C_{l'}HXX...OHA_{n''}$
$\pi''_{l'+m+n''}$ $\pi'''_{l'+m+n''}$

[1] Söldner: Landwirthsch. Versuchstation Bd 35, seperat. 18; quoted after Hammarsten, "Text-book of Physiological Chemistry," trans. by Mandel, 4th ed. (1904) p. 441; Laqueur and Sackur: Hofmeister's Beitr. chem. Physiol., 3, 184; Sackur: Zeit. phys. Chem., 41, 679 (1902); Van Slyke and Hart: Am. Chem. Jour., 33, 461 (1905).

[2] Since one divalent can neutralize two monovalent ampholyte ions the most complex association-salt in this system will be of the order 3η.

Only those equilibrium equations need be discussed which will be actually required in the following investigations:

We have, for equilibrium:

$$ab = K \quad \ldots\ldots(79)$$

$$\left.\begin{aligned} a^3c_1 &= k_a^{(1)}e_1 \\ &\vdots\ \vdots\ \vdots\ \vdots \\ a^3c_n &= k_a^{(n)}e_n \end{aligned}\right\} \quad \ldots\ldots(80)$$

$$\left.\begin{aligned} ac_1''' &= p_a^{(1)}e_1 \\ &\vdots\ \vdots\ \vdots\ \vdots \\ ac_n''' &= p_a^{(1)}e_n \end{aligned}\right\} \quad \ldots\ldots(81)$$

$$\left.\begin{aligned} a\gamma_1 &= \rho_a^{(1)}\theta_1 \\ &\vdots\ \vdots\ \vdots\ \vdots \\ a\gamma_n &= \rho_a^{(n)}\theta_n \end{aligned}\right\} \quad \ldots\ldots(82)$$

$$a^3c'_{m+n''} = r_a^{(m+n'')}\mu_{m+n''} \quad \ldots\ldots(83)$$

$$a^3c''_{m+n''} = q_a^{(m+n'')}\mu'_{m+n''} \quad \ldots\ldots(84)$$

$$ah_{m+n''} = S_a^{(m+n'')}\mu_{m+n''} \quad \ldots\ldots(85)$$

$$ah'_{m+n''} = T_a^{(m+n'')}\mu'_{m+n''} \quad \ldots\ldots(86)$$

$$\left.\begin{aligned} b^2d_1 &= k_b^{(1)}e_1 \\ &\vdots\ \vdots\ \vdots\ \vdots \\ b^2d_n &= k_b^{(n)}e_n \end{aligned}\right\} \quad \ldots\ldots(87)$$

$$\left.\begin{aligned} bd_1''' &= p_b^{(1)}e_1 \\ &\vdots\ \vdots\ \vdots\ \vdots \\ bd_n''' &= p_b^{(n)}e_n \end{aligned}\right\} \quad \ldots\ldots(88)$$

$$\left.\begin{aligned} b\beta_1 &= \rho_b^{(1)}\eta_1 \\ &\vdots\ \vdots\ \vdots\ \vdots \\ b\beta_{n'} &= \rho_b^{(n')}\eta_{n'} \end{aligned}\right\} \quad \ldots\ldots(89)$$

$$b^2d'_{n'+m} = r_b^{(n'+m)}\lambda_{n'+m} \quad \ldots\ldots(90)$$

$$b^2d''_{n'+m} = q_b^{(n'+m)}\lambda'_{n'+m} \quad \ldots\ldots(91)$$

$$bg_{n'+m} = S_b^{(n'+m)}\lambda_{n'+m} \quad \ldots\ldots(92)$$

$$bg'_{n'+m} = T_b^{(n'+m)}\lambda'_{n'+m} \quad \ldots\ldots(93)$$

$$c_n d_m = Q_{n+m} f_{n+m} \quad \ldots\ldots(94)$$

Equating the sums of the concentrations of the ions of opposite signs we have:

$$2a + \sum_{t=1}^{t=n} d_t + 2\sum_{t=1}^{t=n} d''_t + 2\sum_{t=1}^{t=n'} \beta_t + \sum_{t=1}^{t=n'}\sum_{j=1}^{j=n} d'_{t+j} + \sum_{t=1}^{t=n'}\sum_{j=1}^{j=n} d'_{t+j} +$$
$$2\sum_{i=1,j=1}^{i=n'\ j=n} g_{i+j} + 2\sum_{t=1}^{t=n'}\sum_{j=1}^{j=n} g'_{t+j} = 2b + \sum_{t=1}^{t=n} c_t + 2\sum_{t=1}^{t=n} c'''_t + 2\sum_{t=1}^{t=n''} \gamma_t +$$
$$\sum_{t=1}^{t=n}\sum_{j=1}^{j=n''} c'_{t+j} + \sum_{t=1}^{t=n}\sum_{j=1}^{j=n''} c''_{t+j} + 2\sum_{t=1}^{t=n}\sum_{j=1}^{j=n''} h'_{t+j} + 2\sum_{t=1}^{t=n}\sum_{j=1}^{j=n''} h'_{t+j} \quad (95)$$

From (87) we have

$$\sum_{t=1}^{t=n} d_t = \frac{1}{b^2}\sum_{t=1}^{t=n} k_b^{(t)} e_t \quad \ldots\ldots(96)$$

from (88)

$$\sum_{t=1}^{t=n} d''_t = \frac{1}{b}\sum_{t=1}^{t=n} \rho_b^{(t)} e_t \quad \ldots\ldots(97)$$

from (89)

$$\sum_{t=1}^{t=n'} \beta_{n'} = \frac{1}{b}\sum_{t=1}^{t=n'} \rho_b^{(t)} \eta_t \quad \ldots\ldots(98)$$

from (90)

$$\sum_{t=1}^{t=n'}\sum_{j=1}^{j=n} d_{t+j} = \frac{1}{b^2}\sum_{t=1}^{t=n'}\sum_{j=1}^{j=n} r_b^{(t+j)}\lambda_{t+j} \quad \ldots\ldots(99)$$

from (91)

$$\sum_{t=1}^{t=n'}\sum_{j=1}^{j=n} d'_{t+j} = \frac{1}{b^2}\sum_{t=1}^{t=n'}\sum_{j=1}^{j=n} q_b^{(t+j)}\lambda'_{t+j} \quad \ldots\ldots(100)$$

from (92)

$$\sum_{i=1}^{i=n'}\sum_{j=1}^{j=n} g_{i+j} = \frac{1}{b}\sum_{i=1}^{i=n'}\sum_{j=1}^{j=n} S_b^{(i+j)}\lambda_{i+j} \quad \ldots\ldots\ldots\ldots(101)$$

from (93)

$$\sum_{i=1}^{i=n'}\sum_{j=1}^{j=n} g'_{i+j} = \frac{1}{b}\sum_{i=1}^{i=n'}\sum_{j=1}^{j=n} T_b^{(i+j)}\lambda'_{i+j} \quad \ldots\ldots\ldots\ldots(102)$$

from (80)

$$\sum_{i=1}^{i=n} c_i = \frac{1}{a^2}\sum_{i=1}^{i=n} k_a^{(i)} e_i \quad \ldots\ldots\ldots\ldots\ldots\ldots(103)$$

from (81)

$$\sum_{i=1}^{i=n} c'''_n = \frac{1}{a}\sum_{i=1}^{i=n} p_a^{(i)} e_i \quad \ldots\ldots\ldots\ldots\ldots\ldots(104)$$

from (82)

$$\sum_{i=1}^{i=n} \gamma_i = \frac{1}{a}\sum_{i=1}^{i=n} p_a^{(i)}\theta_i \quad \ldots\ldots\ldots\ldots\ldots\ldots(105)$$

from (83)

$$\sum_{i=1}^{i=n}\sum_{j=1}^{j=n''} c'_{i+j} = \frac{1}{a^2}\sum_{i=1}^{i=n}\sum_{j=1}^{j=n''} r_a^{(i+j)}\mu_{i+j} \quad \ldots\ldots\ldots(106)$$

from (84)

$$\sum_{i=1}^{i=n}\sum_{j=1}^{j=n''} c''_{i+j} = \frac{1}{a^2}\sum_{i=1}^{i=n}\sum_{j=1}^{j=n''} q_a^{(i+j)}\mu'_{i+j} \quad \ldots\ldots\ldots(107)$$

from (85)

$$\sum_{i=1}^{i=n}\sum_{j=1}^{j=n''} h_{i+j} = \frac{1}{a}\sum_{i=1}^{i=n}\sum_{j=1}^{j=n''} S_a^{(i+j)}\mu_{i+j} \quad \ldots\ldots\ldots\ldots(108)$$

from (86)

$$\sum_{i=1}^{i=n}\sum_{j=1}^{j=n''} h_{i+j} = \frac{1}{a}\sum_{i=1}^{i=n}\sum_{j=1}^{j=n'} T_a^{(i+j)}\mu'_{(i+j)} \quad \ldots\ldots\ldots(109)$$

Substituting from equations (96–109) in equation (95) we have:

$$2a + \frac{1}{b^2}\sum_{i=1}^{i=n} k_b^{(i)}e_i + \frac{2}{b}\sum_{i=1}^{i=n} p_b^{(i)}e_i + \frac{2}{b}\sum_{i=1}^{i=n'} \rho_b^{(i)}\eta_i + \frac{1}{b^2}\sum_{i=1}^{i=n'}\sum_{j=1}^{j=n} r_b^{(i+j)}\lambda_{i+j}$$

$$+ \frac{1}{b^2}\sum_{i=1}^{i=n'}\sum_{j=1}^{j=n} q_b^{(i+j)}\lambda'_{i+j} + \frac{2}{b}\sum_{i=1}^{i=n'}\sum_{j=1}^{j=n} S_b^{(i+j)}\lambda_{i+j} +$$

$$\frac{2}{b}\sum_{i=1}^{i=n'}\sum_{j=1}^{j=n} T_b^{(i+j)}\lambda'_{i+j} = 2b + \frac{1}{a^2}\sum_{i=1}^{i=n} k_a^{(i)}e_i + \frac{2}{a}\sum_{i=1}^{i=n} p_a^{(i)}e_i +$$

$$\frac{2}{a}\sum_{i=1}^{i=n''} \rho_a^{(i)}\theta_i + \frac{1}{a^2}\sum_{i=1}^{i=n}\sum_{j=1}^{j=n''} r_a^{(i+j)}\mu_{i+j} + \frac{1}{a^2}\sum_{i=1}^{i=n}\sum_{j=1}^{j=n''} q_a^{(i+j)}\mu'_{i+j} +$$

$$\frac{2}{a}\sum_{i=1}^{i=n}\sum_{j=1}^{j=n''} S_a^{(i+j)}\mu_{i+j} + \frac{2}{a}\sum_{i=1}^{i=n}\sum_{j=1}^{j=n''} T_a^{(i+j)}\mu'_{i+j}$$

Multiplying both sides of this equation by a^4b^2, substituting from (79) and rearranging, we have:

$$a^4\left(\sum_{i=1}^{i=n} k_b^{(i)}e_i + \sum_{i=1}^{i=n'}\sum_{j=1}^{j=n} r_b^{(i+j)}\lambda_{i+j} + \sum_{i=1}^{i=n'}\sum_{j=1}^{j=n} q_b^{(i+j)}\lambda'_{i+j}\right) +$$

$$2Ka^3\left(K + \sum_{i=1}^{i=n} p_b^{(i)}e_i + \sum_{i=1}^{i=n'} \rho_b^{(i)}\eta_i + \sum_{i=1}^{i=n'}\sum_{j=1}^{j=n} S_b^{(i+j)}\lambda_{i+j} +\right.$$

$$\left.\sum_{i=1}^{i=n'}\sum_{j=1}^{j=n} T_b^{(i+j)}\lambda'_{i+j}\right) - 2K^2a\left(K + \sum_{i=1}^{i=n} p_a^{(i)}e_i + \sum_{i=1}^{i=n} \rho_a^{(i)}\theta_i +\right.$$

$$\left.\sum_{i=1}^{i=n}\sum_{j=1}^{j=n''} S_a^{(i+j)}\mu_{i+j} + \sum_{i=1}^{i=n}\sum_{j=1}^{j=n''} T_a^{(i+j)}\mu'_{i+j}\right) - K^2\left(\sum_{i=1}^{i=n} k_a^{(i)}e_i +\right.$$

$$\left.\sum_{i=1}^{i=n}\sum_{j=1}^{j=n''} r_a^{(i+j)}\mu_{i+j} + \sum_{i=1}^{i=n}\sum_{j=1}^{j=n''} q_a^{(i+j)}\mu'_{i+j}\right) = 0 \quad \ldots\ldots(110)$$

thus giving a biquadratic in a which, by Descartes' rule of signs, can have only one positive root, so that, just as in the case of system B the variables in this system can be expressed in terms of e_n, $\eta_{n'}$ and $\theta_{n''}$ and of the constants involved.

From (80) and (87) by multiplication and substitution from (79) we have:

$$c_n d_m = \frac{k_a^{(n)} . k_b^{(m)} e_n e_m}{K^2}$$

hence, from (94)

$$\sum_{i=1}^{i=n}\sum_{j=1}^{j=n} Q_{i+j} f_{i+j} = \frac{1}{K^3} \sum_{i=1}^{i=n}\sum_{j=1}^{j=n} k_a^{(i)} k_b^{(j)} e_i e_j \ldots\ldots\ldots (111)$$

hence association increases as dissociation decreases.
From (80)

$$c_n = \frac{k_a^{(n)} e_n}{a^3}$$

from (81)

$$c_n''' = \frac{p_a^{(n)} e_n}{a}$$

from (87)

$$d_n = \frac{k_b^{(n)} e_n}{a^3}$$

and from (88)

$$d_n''' = \frac{p_a^{(n)} e_n}{a}.$$

Hence, and from (79)

$$\frac{d_n + d_n'''}{c_n + c_n'''} = \frac{a^3}{K^3} \cdot \frac{a k_b^{(n)} + K p_b^{(n)}}{k_a^{(n)} + a p_a^{(n)}}.$$

Hence:

$$\sum_{i=1}^{i=n} \frac{d_i + d_i'''}{c_i + c_i'''} = \frac{a^3}{K^3} \sum_{i=1}^{i=n} \frac{a . k_b^{(i)} + K p_b^{(i)}}{k_a^{(i)} + a p_a^{(i)}} \ldots\ldots\ldots (112)$$

Hence the sum of the ratios of the active masses of the dissociated basic ampholates to the active masses of the dissociated acid ampholates increases rapidly with the hydrion concentration, but not according to the simple relation which obtains in systems A and B.

From (80) we have

$$\frac{c_n}{e_n} = \frac{k_a^{(n)}}{a^2}$$

from (81)

$$\frac{c_n'''}{e_n} = \frac{p_a^{(n)}}{a}$$

from (87)

$$\frac{d_n}{e_n} = \frac{k_b^{(n)}}{b^2}$$

and from (88)

$$\frac{d_n'''}{e_n} = \frac{p_b^{(n)}}{b}$$

hence, from (79)

$$\frac{d_n + d_n''' + c_n + c_n'''}{e_n} = \frac{1}{a^2}(k_a^{(n)} + ap_a^{(n)}) + \frac{a}{K^2}(ak_b^{(n)} + Kp_b^{(n)})$$

$$\therefore \sum_{i=1}^{i=n} \frac{d_i + d_i''' + c_i + c_i'''}{e_i} = \frac{1}{K^3a^2}\left\{a^4 \sum_{i=1}^{i=n} k_b^{(i)} + a^3K \sum_{i=1}^{i=n} p_b^{(i)} + aK^2 \sum_{i=1}^{i=n} p_a^{(i)} + K^2 \sum_{i=1}^{i=n} k_a^{(i)}\right\} \quad \ldots\ldots\ldots\ldots (113)$$

Neglecting, for the moment, the formation of *monovalent* ions of the ampholates we see that when a is small the dissociation varies inversely as the *square* of a; similarly, when b is small the dissociation varies *directly* as the square of a.

Differentiating the right-hand side of equation (113) and equating to zero we obtain:

$$2a^4\sum_{i=1}^{i=n}k_b^{(i)}+Ka^3\sum_{i=1}^{i=n}p_b^{(i)}-K^2a\sum_{i=1}^{i=n}p_a^{(i)}-2K^2\sum_{i=1}^{i=n}k_a^{(i)}=0\ldots.(114)$$

a biquadratic equation which, by Descartes' rule of signs, cannot have more than one positive root. A second differentiation shows that this root indicates a minimum of dissociation so long as

$$8a^3\sum_{i=1}^{i=n}k_b^{(i)}+3Ka^2\sum_{i=1}^{i=n}p_b^{(i)}>K^2\sum_{i=1}^{i=n}p_a^{(i)}$$

Assuming that the positive root of equation (114) always indicates a minimum, the same reasoning applies here as in the case of system B, and there will be one "chief" and 2^n-2 "subsidiary" minima of dissociation, any of which may coincide.

From (83)

$$\frac{c'_{m+n''}}{\mu_{m+n''}}=\frac{r_a^{(m+n'')}}{a^2}$$

from (84)

$$\frac{c''_{m+n''}}{\mu'_{m+n''}}=\frac{q_a^{(m+n''}}{a^2}$$

from (85)

$$\frac{h_{m+n''}}{\mu_{m+n''}}=\frac{S_a^{(m+n'')}}{a}$$

from (86)

$$\frac{h'_{m+n''}}{\mu'_{m+n''}}=\frac{T_a^{(m+n'')}}{a}$$

from (90)

$$\frac{d'_{n'+m}}{\lambda_{n'+m}}=\frac{r_b^{(n'+m)}}{b^2}$$

from (91)

$$\frac{d''_{n'+m}}{\lambda'_{n'+m}}=\frac{q_b^{(n'+m)}}{b^2}$$

from (92)

$$\frac{g_{n'+m}}{\lambda_{n'+m}} = \frac{S_b^{(n'+m)}}{b}$$

and from (93)

$$\frac{g'_{n'+m}}{\lambda'_{n'+m}} = \frac{T_b^{(n'+m)}}{b}.$$

Hence, by addition

$$\sum_{i=1}^{i=n}\sum_{j=1}^{j=n''}\frac{c'_{i+j}+h_{i+j}}{\mu_{i+j}}+\sum_{i=1}^{i=n}\sum_{j=1}^{j=n''}\frac{c''_{i+j}+h'_{i+j}}{\mu'_{i+j}}+\sum_{i=1}^{i=n'}\sum_{j=1}^{j=n}\frac{d'_{i+j}+g_{i+j}}{\lambda_{i+j}}$$
$$+\sum_{i=1}^{i=n'}\sum_{j=1}^{j=n}\frac{d''_{i+j}+g'_{i+j}}{\lambda'_{i+j}}=\frac{1}{K^2a^3}\Bigg\{a^4\Bigg(\sum_{i=1}^{i=n'}\sum_{i=1}^{i=n}r_b^{(i+j)}+$$
$$\sum_{i=1}^{i=n'}\sum_{j=1}^{j=n}q_b^{(i+j)}\Bigg)+Ka^3\Bigg(\sum_{i=1}^{i=n'}\sum_{j=1}^{j=n}S_b^{i+j}+\sum_{i=1}^{i=n'}\sum_{j=1}^{j=n}T_b^{(i+j)}\Bigg)+$$
$$K^3a\Bigg(\sum_{i=1}^{i=n}\sum_{j=1}^{j=n''}S_a^{(i+j)}+\sum_{i=1}^{i=n}\sum_{j=1}^{j=n''}T_a^{(i+j)}\Bigg)+$$
$$K^2\Bigg(\sum_{i=1}^{i=n}\sum_{j=1}^{j=n''}r_a^{(i+j)}+\sum_{i=1}^{i=n}\sum_{j=1}^{j=n''}q_a^{(i+j)}\Bigg)\Bigg\}\ldots\ldots\ldots(115)$$

The left-hand side of this equation is the sum of the ratios of the masses of the dissociated acid and basic ampho-salts to the masses of the undissociated ampho-salts. Differentiating the right-hand side of the equation and equating to zero we have the biquadratic:

$$2a^4\Bigg(\sum_{i=1}^{i=n'}\sum_{j=1}^{j=n}r_b^{(i+j)}+\sum_{i=1}^{i=n'}\sum_{j=1}^{j=n}q_b^{(i+j)}\Bigg)+Ka^3\Bigg(\sum_{i=1}^{i=n'}\sum_{j=1}^{j=n}S_b^{(i+j)}+$$
$$\sum_{i=1}^{i=n'}\sum_{j=1}^{j=n}T_b^{(i+j)}\Bigg)-K^2a\Bigg(\sum_{i=1}^{i=n}\sum_{j=1}^{j=n''}S_a^{(i+j)}+\sum_{i=1}^{i=n}\sum_{j=1}^{j=n''}T_a^{(i+j)}\Bigg)-$$
$$2K^3\Bigg(\sum_{i=1}^{i=n}\sum_{j=1}^{j=n''}r_a^{(i+j)}+\sum_{i=1}^{i=n}\sum_{j=1}^{j=n''}q_a^{(i+j)}\Bigg)=0$$

which, by Descartes' rule of signs, can have only one positive root. Differentiating a second time we see that this positive root indicates a minimum so long as

$$8a^3\left(\sum_{i=1}^{i=n'}\sum_{j=1}^{j=n}\gamma_b^{(i+j)}+\sum_{i=1}^{i=n'}\sum_{j=1}^{j=n}q_b^{(i+j)}\right)+3Ka^2\left(\sum_{i=1}^{i=n'}\sum_{j=1}^{j=n}S_b^{(i+j)}+\sum_{i=1}^{i=n'}\sum_{j=1}^{j=n}T_b^{(i+j)}\right)>K^3\left(\sum_{i=1}^{i=n}\sum_{j=1}^{j=n''}S_a^{(i+j)}+\sum_{i=1}^{i=n}\sum_{j=1}^{j=n''}T_a^{(i+j)}\right).$$

Applying similar reasoning to that employed in the case of the system B, there will be one "chief" minimum of dissociation of the acid and basic ampho-salts and $2^{n'n''n'''}-2$ "subsidiary" minima, some or any of which may coincide. As in system B, also, when the dissociation of the ampho-salts is at a minimum, association will be at a maximum.

E. The Conditions of Equilibrium of an Associating Ampholyte, the Ions of Which Are All Univalent, in the Presence of Any Number of Non-Amphoteric Electrolytes, the Ions of Which Are Partly Univalent and Partly Divalent

Let the masses of the various substances in equilibrium be represented as follows:

H^+	OH'	$XX\ldots.OH'$	$HX\ldots.X^+$	$HX\ldots.XOH$	$XX\ldots.X$	
a	b	c_n	d_n	e_n	f_{2n}	
$C^+_{n'}$	$M^{+++}_{n'''}$	$A'_{n''}$	$N''_n{}^{iv}$	$C_{n'}A_{m''}$	$M_{n'''}N_m{}^{iv}$	$C_{n'}OH$
$\beta_{n'}$	$\phi_{n'''}$	$\gamma_{n''}$	$\omega_n{}^{iv}$	$\delta_{n'+m''}$		$\eta_{n'}$
$A_{n''}H$	$M_{n'''}(OH)_2$	$N_n{}^{iv}H_2$	$C_{n'}XX\ldots.X^+$	$XX\ldots.A'_{n''}$		
$\theta_{n''}$	$\eta'_{n'''}$	$\theta'_n{}^{iv}$	$d'_{n'+m}$	$c'_{m+n''}$		
$M_{n'''}XX\ldots.X^{++}$	$XX\ldots.N''_n{}^{iv}$	$M_{p'''}X\ldots.XA^+_{n''}$	$M_{p'''}X\ldots.XOH^+$			
$d''_{n'''+m}$	$c''_{m+n}{}^{iv}$	$g_{p'''+m+n''}$	$g'_{p'''+m}$			
$C_pXX\ldots.N'_n{}^{iv}$	$HXX\ldots.N'_n{}^{iv}$	$HXX\ldots.A_{n''}$	$C_{n'}X\ldots.XOH$			
$h_{p+m+n}{}^{iv}$	$h'_{m+n}{}^{iv}$	$\mu_{m+n''}$	$\lambda_{n'+m}$			
$H_2XX\ldots.N_n{}^{iv}$	$M_{n'''}X\ldots.X(OH)_2$	$M_{p'''}X\ldots.XA_{n''}OH$				
$\mu'_{m+n}{}^{iv}$	$\lambda'_{n'''+m}$	$\chi'_{p'''+m+n''}$				

$HC_pX....XN_{n^{iv}}$ $C_pX....XA_{n''}$ $M_{p'''}X....XN_{n^{iv}}$

$X_{p+m+n^{iv}}$

$M_{p'''}X....X(A_{n''})_2$ $(C_p)_2X....XN_{n^{iv}}$

Considering only those equations which will be required in the following investigation we have:

$$ab = K \quad \ldots\ldots(116)$$

$$ac_n = k_a^{(n)} e_n \quad \ldots\ldots(117)$$

$$a\gamma_{n''} = \rho_a^{(n'')} \theta_{n''} \quad \ldots\ldots(118)$$

$$a^2\omega_{n^{iv}} = \zeta_a^{(n^{iv})} \theta'_{n^{iv}} \quad \ldots\ldots(119)$$

$$ac'_{m+n''} = r_a^{(m+n'')} \mu_{m+n''} \quad \ldots\ldots(120)$$

$$a^2c''_{m+n^{iv}} = p_a^{(m+n^{iv})} \mu'_{m+n^{iv}} \quad \ldots\ldots(121)$$

$$ah_{p+m+n^{iv}} = q_a^{(p+m+n^{iv})} \chi_{p+m+n^{iv}} \quad \ldots\ldots(122)$$

$$ah'_{m+n^{iv}} = S_a^{(m+n^{iv})} \mu'_{m+n^{iv}} \quad \ldots\ldots(123)$$

$$bd_n = k_b^{(n)} e_n \quad \ldots\ldots(124)$$

$$b\beta_{n'} = \rho_b^{(n')} \eta_{n'} \quad \ldots\ldots(125)$$

$$b^2\phi_{n'''} = \zeta_b^{(n''')} \eta'_{n'''} \quad \ldots\ldots(126)$$

$$bd'_{n'+m} = r_b^{(n'+m)} \lambda_{n'+m} \quad \ldots\ldots(127)$$

$$b^2d''_{n'''+m} = p_b^{(n'''+m)} \lambda'_{n'''+m} \quad \ldots\ldots(128)$$

$$bg_{p'''+m+n''} = q_b^{(p'''+m+n'')} \chi_{p'''+m+n''} \quad \ldots\ldots(129)$$

$$bg'_{p'''+m} = S_b^{(p'''+m)} \lambda'_{p'''+m} \quad \ldots\ldots(130)$$

The solution for a, as in system D, gives a biquadratic. From (124)

$$d_n = \frac{k_b^{(n)} e_n}{b} \quad \ldots\ldots(131)$$

and from (117)

$$c_n = \frac{k_a^{(n)} e_n}{a} \quad \ldots\ldots(132)$$

∴ from (116)

$$\frac{d_n}{c_n} = \frac{k_b^{(n)}}{k_a^{(n)}} \cdot \frac{a^2}{K}$$

$$\therefore \sum_{i=1}^{i=n} \frac{d_i}{c_i} = \frac{a^2}{K} \sum_{i=1}^{i=n} \frac{k_b^{(i)}}{k_a^{(i)}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (133)$$

Hence, as in systems A and B, *the sum of the ratios of the active masses of the dissociated basic ampholates to the active masses of the dissociated acid ampholates varies as the square of the hydrion concentration.* Similarly, the sum of the ratios of the active masses of the dissociated acid ampholates to the active masses of the dissociated basic ampholates varies as the square of the hydroxidion concentration just as in system B, also, we have:

$$\sum_{i=1}^{i=n} \frac{d_i + c_i}{e_i} = \frac{1}{Ka} \left(K \sum_{i=1}^{i=n} k_a^{(i)} + a^2 \sum k_b^{(i)} \right) \ldots\ldots (134)$$

hence when a is small the dissociation of the ampholates varies inversely as a, that is, from (116), directly as b, while when b is small the dissociation varies directly as a and inversely as b. The quantity $\sum_{i=1}^{i=n} \frac{d_i + c_i}{e_i}$ is at a minimum when $a^2 = K \frac{\sum_{i=1}^{i=n} k_a^{(i)}}{\sum_{i=1}^{i=n} k_b^{(i)}}$, at which hydrion concentration the sum of the active masses of the dissociated basic ampholates is equal to the sum of the active masses of the dissociated acid ampholates, that is, probably, the ampholyte is "iso-electric" or, in other words, does not move in either direction in an electric field. As in system B, when dissociation of the ampholates is at a minimum, association is at a maximum and there will be one "chief" minimum of dissociation of the

ampholates and $2''-2$ "subsidiary" minima which may coincide.

From (120)

$$\frac{c'_{m+n''}}{\mu_{m+n''}} = \frac{r_a^{(m+n'')}}{a}$$

from (121)

$$\frac{c''_{m+n^{iv}}}{\mu'_{m+n^{iv}}} = \frac{p_a^{(m+n^{iv})}}{a^2}$$

from (122)

$$\frac{h_{r+m+n^{iv}}}{\chi_{r+m+n^{iv}}} = \frac{q_a^{(r+m+n^{iv})}}{a}$$

from (123)

$$\frac{h'_{m+n^{iv}}}{\mu'_{m+n^{iv}}} = \frac{S_a^{(m+n^{iv})}}{a}$$

from (127) and (116)

$$\frac{d'_{n'+m}}{\lambda_{n'+m}} = \frac{r_b^{(n'+m)}}{K} \cdot a$$

from (128) and (116)

$$\frac{d''_{n'''+m}}{\lambda'_{n'''+m}} = \frac{p_b^{(n'''+m)}}{K^2} a^2$$

from (129) and (116)

$$\frac{g_{r''+m+n''}}{\chi'_{r''+m+n''}} = \frac{q^{(r''+m+n'')}}{K} \cdot a$$

and from (130) and (116)

$$\frac{g_{n'''+m}}{\lambda'_{n'''+m}} = \frac{S_b^{(n'''+m)}}{K} \cdot a$$

hence, by addition

$$\sum_{i=1}^{i=n}\sum_{j=1}^{j=n''}\frac{c'_{i+j}}{\mu_{i+j}}+\sum_{i=1}^{i=n}\sum_{j=1}^{j=n^{iv}}\frac{c''_{i+j}+h'_{i+j}}{\mu'_{i+j}}+\sum_{i=1}^{i=n'}\sum_{j=1}^{j=n}\sum_{k=1}^{k=n^{iv}}\frac{h_{i+j+k}}{\chi_{i+j+k}}+$$

$$\sum_{i=1}^{i=n'}\sum_{j=1}^{j=n}\frac{d_{i+j}}{\lambda_{i+j}}+\sum_{i=1}^{i=n'''}\sum_{j=1}^{j=n}\frac{d''_{i+j}+g'_{i+j}}{\lambda'_{i+j}}+\sum_{i=1}^{i=n'''}\sum_{j=1}^{j=n}\sum_{k=1}^{k=n''}\frac{g_{i+j+k}}{\chi'_{i+j+k}}=$$

$$\frac{a^2}{K^2}\sum_{i=1}^{i=n'''}\sum_{j=1}^{j=n}p_b^{(i+j)}+\frac{a}{K}\left(\sum_{i=1}^{i=n'}\sum_{j=1}^{j=n}r_b^{(i+j)}+\sum_{i=1}^{i=n'''}\sum_{j=1}^{j=n}\sum_{k=1}^{k=n''}q_b^{(i+j+k)}+\right.$$

$$\left.\sum_{i=1}^{i=n'''}\sum_{j=1}^{j=n}S_b^{(i+j)}\right)+\frac{1}{a}\left(\sum_{i=1}^{i=n}\sum_{j=1}^{j=n''}r_a^{(i+j)}+\sum_{i=1}^{i=n'}\sum_{j=1}^{j=n}\sum_{k=1}^{k=n^{iv}}q_a^{(i+j+k)}+\right.$$

$$\left.\sum_{i=1}^{i=n}\sum_{j=1}^{j=n^{iv}}S_a^{(i+j)}\right)+\frac{1}{a^2}\sum_{i=1}^{i=n}\sum_{j=1}^{j=n^{iv}}p_a^{(i+j)}\quad\ldots\ldots\ldots\ldots(135)$$

Putting the left-hand side of the equation equal to D we have:

$$D=\frac{1}{a^2K^2}\left\{a^4\sum_{i=1}^{i=n'''}\sum_{j=1}^{j=n}p_b^{(i+j)}+a^3K\left(\sum_{i=1}^{i=n'}\sum_{j=1}^{j=n}r_b^{(i+j)}+\right.\right.$$

$$\sum_{i=1}^{i=n'''}\sum_{j=1}^{j=n}\sum_{k=1}^{k=n''}q_b^{(i+j+k)}+\left.\sum_{i=1}^{i=n'''}\sum_{j=1}^{j=n}S_b^{(i+j)}\right)+aK^2\left(\sum_{i=1}^{i=n}\sum_{j=1}^{j=n''}r_a^{(i+j)}+\right.$$

$$\sum_{i=1}^{i=n'}\sum_{j=1}^{j=n}\sum_{k=1}^{k=n^{iv}}q_a^{(i+j+k)}+\left.\sum_{i=1}^{i=n}\sum_{j=1}^{j=n^{iv}}S_a^{(i+j)}\right)+$$

$$\left.K^3\sum_{i=1}^{i=n}\sum_{j=1}^{j=n^{iv}}p_a^{(i+j)}\right\}\quad\ldots\ldots\ldots\ldots\ldots\ldots(136)$$

which expresses the dissociation of the acid and basic amphosalts in terms of the hydrion concentration and of the constants involved.

Equation (135) may also be written, by substituting from equations (119), (118), (125) and (126).

$$D = \frac{1}{K^3}\frac{\sum_{i=1}^{i=n^{iv}}\xi_a^{(i)}\theta'_i}{\sum_{i=1}^{i=n^{iv}}\omega_i}\sum_{i=1}^{i=n'''}\sum_{j=1}^{j=n}p_b^{(i+j)} + \frac{1}{K}\frac{\sum_{i=1}^{i=n''}\rho_a^{(i)}\theta_i}{\sum_{i=1}^{i=n''}\gamma_i}\left(\sum_{i=1}^{i=n'}\sum_{j=1}^{j=n}r_b^{(i+j)} + \sum_{i=1}^{i=n'''}\sum_{j=1}^{j=n}\sum_{k=1}^{k=n''}q_b^{(i+j+k)} + \sum_{i=1}^{i=n'''}\sum_{j=1}^{j=n}S_b^{(i+j)}\right) +$$

$$\frac{1}{K}\frac{\sum_{i=1}^{i=n'}\rho_b^{(i)}\eta_i}{\sum_{i=1}^{i=n'}\beta_i}\left(\sum_{i=1}^{i=n}\sum_{j=1}^{j=n''}r_a^{(i+j)} + \sum_{i=1}^{i=n'}\sum_{j=1}^{j=n}\sum_{k=1}^{k=n^{iv}}q_a^{(i+j+k)} + \sum_{i=1}^{i=n}\sum_{j=1}^{j=n^{iv}}S_a^{(i+j)}\right) + \frac{1}{K^2}\frac{\sum_{i=1}^{i=n'''}\zeta_b^{(i)}\eta'_i}{\sum_{i=1}^{i=n'''}\phi_i}\sum_{i=1}^{i=n}\sum_{j=1}^{j=n^{iv}}p_a^{(i+j)} \quad \ldots\ldots\ldots\ldots\ldots\ldots (137)$$

Since the coefficients of the quantities expressing the dissociation of the non-amphoteric univalent acids and bases in the above equation involve constants depending upon the relations between the *divalent* ions present and the ampholyte the solvent powers of the different salts will not, in general, be additive. If, however, the non-amphoteric ions present in the system (except hydrion and hydroxidion) be *all monovalent or all divalent* the solvent powers of the different salts will clearly be additive. Connected with this may possibly be the fact that in the case of globulin, which combines with acids and bases in *molecular* proportions, so that its solution in salts forms a system comparable with system B irrespective of the valency of the ions of the salts, the solvent powers of different salts, whether monovalent or divalent, are additive, whereas Picton and Linder found that the precipitating power of salts was only additive when the ions of the salts were of the same valency.[1]

[1] W. B. Hardy: Jour. Physiol., 33, 313 (1905).

Differentiating the right-hand side of equation (135) and equating to zero we have:

$$2a^4\sum_{i=1}^{i=n'''}\sum_{j=1}^{j=n} p_b^{(i+j)} + \mathrm{K}a^3\Big(\sum_{i=1}^{i=n'}\sum_{j=1}^{j=n} r_b^{(i+j)} + \sum_{i=1}^{i=n'''}\sum_{j=1}^{j=n}\sum_{k=1}^{k=n''} q_b^{(i+j+k)} + \sum_{i=1}^{i=n'''}\sum_{j=1}^{j=n} \mathrm{S}_b^{(i+j)}\Big) - \mathrm{K}^2a\Big(\sum_{i=1}^{i=n}\sum_{j=1}^{j=n''} r_a^{(i+j)} + \sum_{i=1}^{i=n'}\sum_{j=1}^{j=n}\sum_{k=1}^{k=n^{\mathrm{iv}}} q_a^{(i+j+k)} + \sum_{i=1}^{i=n}\sum_{j=1}^{j=n^{\mathrm{iv}}} \mathrm{S}_a^{(i+j)}\Big) - 2\mathrm{K}^3\sum_{i=1}^{i=n}\sum_{j=1}^{j=n^{\mathrm{iv}}} p_a^{(i+j)} = 0$$

an equation in a which, by Descartes' rule of signs, can have only one positive root which will indicate a minimum of dissociation so long as

$$8a^3\sum_{i=1}^{i=n'''}\sum_{j=1}^{j=n} p_b^{(i+j)} + 3\mathrm{K}a^2\Big(\sum_{i=1}^{i=n'}\sum_{j=1}^{j=n} r_b^{(i+j)} + \sum_{i=1}^{i=n'''}\sum_{j=1}^{j=n}\sum_{k=1}^{k=n''} q_b^{(i+j+k)} + \sum_{i=1}^{i=n'''}\sum_{j=1}^{j=n} \mathrm{S}_b^{(i+j)}\Big) > \mathrm{K}^2\Big(\sum_{i=1}^{i=n}\sum_{j=1}^{j=n'} r_a^{(i+j)} + \sum_{i=1}^{i=n'}\sum_{j=1}^{j=n}\sum_{k=1}^{k=n^{\mathrm{iv}}} q_a^{(i+j+k)} + \sum_{i=1}^{i=n}\sum_{j=1}^{j=n^{\mathrm{iv}}} \mathrm{S}_a^{(i+j)}\Big)$$

If there be present n orders of ampholates, n' non-amphoteric univalent cations, n''' non-amphoteric divalent cations, n'' non-amphoteric univalent anions, and n^{iv} non-amphoteric divalent anions, the total number of acid ampho-salts will be $n(n''+2n^{\mathrm{iv}}+n'n^{\mathrm{iv}})$ while the total number of basic ampho-salts will be $n(n'+2n'''+n'''n'')$, so that the total number of pairs of acid and basic ampho-salts will be:

$$n^2(n' + 2n''' + n'''n'')(n'' + 2n^{\mathrm{iv}}n + n'n^{\mathrm{iv}})$$

and the total number of minima of dissociation of one or more pairs of ampho-salts will be:

$$2^{n^2(n' + 2n''' + n'''n'')(n'' + 2n^{\mathrm{iv}} + n'n^{\mathrm{iv}})} - 1$$

of which one will be "chief" and the remainder "subsidiary."

Hence the number of minima of dissociation of the acid and basic ampho-salts *increases very rapidly with increasing valency of the non-amphoteric ions*. And, be it noted, this holds good whether the ampholyte belongs to Class I or to Class II for the number of minima of dissociation of the ampho-salts obviously depends solely upon the number of *species* of ions present and not upon their stoichiometrical relations.

If only one non-amphoteric salt, composed of univalent ions, be present in the system the number of minima of dissociation of the ampho-salts, as the concentration of the non-amphoteric salt varies, will be $2^{n^2}-1$ if n be the number of ampholates present. If, however, the non-amphoteric salt be composed of divalent ions the number of minima will be $2^{4n^2}-1$. Now the chance of any given concentration of a salt precipitating an ampholyte obviously varies directly as the number of minima of dissociation induced in the ampholyte by varying concentrations of the salt, that is, the precipitating power of a salt composed of univalent ions will be to the precipitating power of an equivalent concentration of a salt of divalent ions as $\frac{2^{n^2}-1}{2^{4n^2}-1}$, that is, *if n be large*, as 1 is to 16. This may possibly afford an alternative explanation to that offered by Whetham[1] of the remarkable relation between the precipitating power of a salt for colloids and the valency of its ions which obtains in certain classes of precipitations of colloids (namely the *third* class of precipitation discussed on p. 555 due to an approaching of the "chief" minimum of dissociation of the ampho-salts).

III. Connection between This Investigation and the Ion-proteid Hypothesis

The ion-proteid hypothesis, as suggested by Loeb[2] and by Pauli,[3] is that the ions of an electrolyte, on diffusing into a

[1] W. C. D. Whetham in a note in a paper by W. B. Hardy: Jour. Physiol., 24, 288 (1899); see also W. C. D. Whetham: Phil. Mag. [5], 48, 474 (1899).

[2] J. Loeb: Am. Jour. Physiol., 3, 327 (1900).

[3] W. Pauli: "Ueber physikalisch-chemische Methoden und Probleme in der Medizin," Wien, 1900.

tissue, enter into combination with some constituents of the tissue, presumably proteids. This hypothesis was based upon the fact, established by the researches of Dreser,[1] on the toxicity of salts of mercury, of Klemm,[2] and of Kahlenberg and True,[3] on the toxicity of acids and alkalies, of Heald [4] and of Maillard,[5] on the toxicity of salts of copper, of Paul and Krönig,[6] on the disinfectant action of salts of heavy metals, and of Loeb,[7] on the swelling of muscles in solutions of acids, that the influence of an electrolyte upon a tissue was directly dependent upon its degree of ionization. Subsequent researches have tended to confirm the idea of the importance of the degree of dissociation of an electrolyte in determining its effect upon tissues although a direct dependence cannot invariably be predicated.

Early last year I utilized the ion-proteid hypothesis in attempting to offer an explanation of the phenomena of protoplasmic motion and excitation[8] and I suggested that the nature of the ion-proteid formed in general under the influence of an electrolyte is determined by the velocities of the ions into which the electrolyte is dissociated, for the swifter moving ions would enter the tissue in larger quantities and the potential difference which would thus tend to be set up between the tissue and the solution would be annulled, so far as the ions which actually combine are concerned, by the simultaneous splitting off from the protein of hydrogen or hydroxyl ions of opposite electrical sign, while the ions present in the greatest mass might be expected to take the greater

[1] Dreser: Arch. f. Exper. Path. und Pharmakol., 32, 456 (1893).

[2] Klemm: Jahrb. f. wiss. Botanik, 28, 658 (1895).

[3] Kahlenberg and True: Botanical Gazette, 22, No. 2, p. 81.

[4] Heald: Ibid., 22, No. 2, p. 125.

[5] Maillard: C. r. Soc. de Biol. [10], 5, 1210 (1898); Jour. de Physiol. et de Path. Gén., 1, 651, 673.

[6] Paul and Krönig: Zeit. phys. Chem., 21, 414 (1896); also Zeit. für Hygiene, 25, 1 (1897).

[7] Loeb: Pflügers Arch. f. d. ges. Physiol., 69, 1 (1898).

[8] Trans. Roy. Soc. South Australia, 29, 1 (1905); see also Pflüger's Arch. f. d. ges. Physiol., 110, 610 (1905); Biol. Bulletin, 11, 53 (1906).

share of the protein. In subsequent papers[1] I pointed out that if this hypothesis were correct we should expect a tissue immersed in a solution of an electrolyte in which the cation had the higher velocity to become predominantly basic in character while in a solution of an electrolyte in which the anion had the higher velocity the tissue would become predominantly acid, and I showed that in solutions in which the cation has the higher velocity a tissue is stained deeply by color-acids, faintly by color-bases, whereas in solutions in which the anion has the higher velocity the reverse is the case. Similarly, alkaloids which are purely basic in character show a maximum of toxicity when acting in solutions of electrolytes in which the anion has the higher velocity, while alkaloids which possess both acid and basic properties show two maxima of toxicity, the one in solutions in which the anion has the higher velocity, the other in solutions in which the cation has the higher velocity—results which, assuming that the staining of a tissue by a dye, on the one hand, and the toxic action of an alkaloid, on the other, depend upon the formation of a chemical compound between the proteins in the tissue and the dye or alkaloid, are completely in harmony with the hypothesis. So far, however, no definite assumption has been made as to the chemical nature of the ion-proteid compounds although Loeb pointed out the analogy with soaps[2] and, later, with amido-acid compounds.[3] Empirically, however, we appear to have sufficient evidence to state that the ions of an electrolyte on diffusing into a tissue form loose compounds there in which one ion is readily replaceable by another (except in certain cases, *e. g.*, the heavy metal salts), that the ions present in a tissue in the greatest mass form, in general, the greater part of the ion-proteids and that when the ions present in the tissue in the greatest mass are anions the tissue has in general predominantly acid properties, while when the ions present in the tissue in the greatest mass are cations the tissue has predominantly basic properties.

[1] Jour. Biol. Chem., 1, 279, 507 (1906).
[2] J. Loeb: Pflüger's Arch. f. d. ges. Physiol., 75, 303 (1899).
[3] J. Loeb: Am. Jour. Physiol., 3, 327 (1900).

Now a moment's consideration of equations (59), (112) and (133) will show that in the presence of excess of anions an ampholyte must assume predominantly acid characters while in the presence of excess of cations it must assume predominantly basic characters, for an excess of anions will diminish the dissociation of the non-amphoteric acids and diminish the hydrion concentration, thus increasing the proportion of the ampholates dissociating as acids. Moreover, the ampho-salts will mainly contain non-amphoteric anions and so will tend to dissociate as acids. In the same way excess of cations would increase the basic properties of the ampholyte. An ampholyte system also obviously possesses the other properties which have been ascribed to the ion-proteids. Since, as I have pointed out in the introduction, we know that proteins are amphoteric electrolytes and that they combine with non-amphoteric acids, bases, and, probably, salts, and we have seen that an ampholyte system possesses the properties which have been ascribed to the ion-proteids, we are, I think, justified in making the following assumptions:

(1) That the compounds which have been termed "ion-proteids" are, in reality, ampho-salts of the proteins (*e. g.*, NaXOH,HXCl).

(2) That the non-dissociable compounds of protein with non-amphoteric ions, which exist in tissues, are, in reality, ampho-salts dissociating as acids and bases or else di-salts (*e. g.*, $NaX^+ + OH'$, $H^+ + XCl'$ or NaXCl).

(3) That the influence of electrolytes upon the properties and reactions of tissues may probably be referred, in the main, to alterations in the ratio of the basic ampholates (*e. g.*, $HX^+ + OH'$) to the acid ampholates (*e. g.*, $H^+ + XOH'$) and to the formation of ampho-salts and di-salts.

Incidentally, I may here point out that the fact pointed out by Bugarszky and Liebermann[1] and others, to which I have referred in the introduction, that proteins, added to

[1] Bugarszky and Liebermann: Pflüger's Arch. f. d. ges. Physiol., 72, 51 (1898).

solutions of "neutral salts," do not depress the electric conductivity of the solutions to any appreciable extent, which has constituted an obstacle to the ion-proteid theory, meets with a simple explanation on the basis of the ampholyte hypothesis as outlined above, for in a solution of a "neutral salt" the acid and basic ampholates would, unless the acid or basic function predominated to a marked extent, be very nearly balanced—so that both would be weak and, in the case of NaCl for example, although the base NaOH would be shared between the acid ampholate and the HCl, yet the latter would take the very *much* greater share. Hence, at any given concentration of NaCl the amount actually combined with the protein would be a very small proportion of the whole.

IV. Summary

(1) In the introduction the successes and failures in the attempt to discover simple stoichiometrical relations in protein systems have been briefly reviewed, and it has been suggested that the successes are possibly particular cases of some more general relations and that these more general relations may be ascertained by a study of the equilibrium conditions of an associating amphoteric electrolyte. In the introduction, also, the terms "ampholyte," "ampholate," "ampho-salt" "basic" and "acid" ampho-salt, "di-salt, "and "association salt" are defined.

(2) In Part II the conditions of equilibrium in the systems A, B, C, D, and E are discussed. In connection with system D it is pointed out that proteins, as regards valency relations, may be divided into Class I, to which *e. g.*, globulin belongs, and Class II to which *e. g.*, casein belongs. Proteins of Class I in the presence of any electrolytes, whether univalent or divalent, may be regarded as forming a system B. Proteins of Class II form, in addition to system B, systems D and E. Applications to solubility-phenomena in proteins are discussed in connection with system B and agreements between theory and experiment established as regards swelling

phenomena, etc. In connection with system E the conditions under which the solvent powers of salts may be expected to be additive are discussed and also a suggestion offered in regard to the relation between the valency and precipitating power of non-amphoteric ions.

(3) In connection with system C it is pointed out that in order that Guldberg and Waage's mass law may be directly applied to the reaction between two different associating ampholytes (amphoteric electrolytes), *one of the reacting ampholytes must be "iso-electric" and must remain so throughout the reaction*, or else the acid function of the one and the basic function of the other must be negligible.

(4) In Part III the connection between this investigation and the ion-proteid hypothesis is discussed, and the hypothesis is advanced that the compounds which have been termed ion-proteids are, in reality, ampho-salts of the proteins, that the non-dissociable ion-proteid compounds are ampho-salts dissociating as acids and bases, or else di-salts, and that the influence of electrolytes upon the properties and reactions of tissues may possibly be largely attributed to alterations in the equilibria discussed in this paper.

NEW BOOKS

The Dynamics of Living Matter. *By Jacques Loeb. 16 × 23 cm; pp. xi + 233. New York: The Macmillan Company, 1906. Price: bound, $3.00.*—The book is based on a course of lectures given at Columbia University in 1902. The subjects of the lectures are: general chemistry of life phenomena; general physical constitution of living matter; some physical manifestations of life; the rôle of electrolytes in the formation and preservation of living matter; the effects of heat and radiant energy upon living matter; heliotropism; further facts concerning tropisms and related phenomena; fertilization; heredity; the dynamics of regenerative processes.

The most striking characteristic of the chemistry of life is that we are dealing with catalytic reactions, the living matter manufacturing its own catalyzers. Respiration is to be looked upon as a catalytic process involving the taking up of oxygen and the giving off of carbon dioxide. The mere performance of certain chemical reactions does not, however, suffice to define living matter. In addition we must have a definite physical structure and this appears to involve a limited divisibility. While some cells can be split into two or more parts and yet have each part develop, this is no longer true if we make eight or sixteen divisions.

The physical structure of living matter is apparently a question coming under the heading of the physics of colloids. Bütschli, for instance, considers that living protoplasm has the structure of a microscopic emulsion. This view is not accepted unconditionally by everybody; but it is in harmony with a great many facts. While many animal membranes appear to be more or less completely semipermeable, the general theory of osmotic pressure does not seem to apply in the case of *Fundulus* which will live either in sea water or in distilled water. The many cases, in which definite concentrations of certain salts are necessary, show that the chemical reactions of these salts with the protoplasmic material inside the cells is of great importance. This receives further confirmation from the behavior of so-called protective solutions and from the action of certain salts in producing rhythmical contractions.

After producing rhythmical contractions in a so-called dead heart by chemical methods, Loeb shows that the rate of contraction varies with the temperature in accordance with the usual formula for change of reaction velocity with the temperature. The development of unfertilized eggs by purely chemical methods and the proof that the various forms of tropisms are purely automatic are specially interesting to the chemist as showing the part that chemistry is to play in the biology of the immediate future.

The last two lectures are on heredity and on the dynamics of regenerative processes. While these are distinctly more biological than chemical, it is interesting to note how much clearer the conceptions become when an author takes the chemical and physical phenomena into account.

There is one point which chemists usually overlook and which is brought out very clearly in this book. It is not possible to explain all secretions and absorptions of liquids by means of osmotic pressure. If we stop for a moment

to think about this, we shall realize that we have always known this though we have not always kept it in mind. If a man gets a grain of sand in his eye, he will weep; but this secretion does not decrease the osmotic pressure outside the eyeball because the sand does not dissolve. This is a secretion due to irritation. In this case any one can see that osmotic pressure is not an important factor; but it now becomes necessary for us to prove, in any given case, that a secretion or absorption is due to osmotic pressure and not to irritation or some other cause.

Wilder D. Bancroft

Higher Mathematics for Students of Chemistry and Physics, with Special Reference to Practical Work. *By J. W. Mellor. Second edition, enlarged. 14 × 22 cm; pp. xv + 631. New York: Longmans, Green and Co., 1905. Price: bound, $4.50.*—The fact that Mellor's Higher Mathematics has gone into a second edition is evidence that it meets a real want. Of the present edition it is stated that the subject-matter has been rewritten, and that many parts have been extended in order to meet the growing tendency on the part of physical chemists to describe their ideas in the unequivocal language of mathematics. The author's description of his book is interesting. He calls it an introduction to the mathematical treatment of the hypotheses and measurements employed in scientific work. That the book may be thus described is probably the reason for its success. Its eleven chapters present a lot of mathematics: differential calculus, analytic geometry, functions with singular properties, integral calculus, series, the solution of numerical equations, differential equations, Fourier's theorem, probability and theory of errors, calculus of variations, and determinants. Much useful matter, too, is included in the appendices. A fairly large volume is the result, but no one topic in it is unduly expanded, and its range makes it an admirable work of reference for the man who learns his mathematics as he goes. Being well written, in a friendly and conversational style, clearly printed, and well indexed at both ends, the book deserves its past success and cordial good wishes for its future.

J. E. Trevor

Lehrbuch der Physik, zum Gebrauche bei akademischen Vorlesungen. *By H. A. Lorentz. Erster Band. Nach der vierten, von H. A. Lorentz und L. H. Siertsema bearbeiteten Auflage, und unter Mitwirkung des Verfassers, aus dem holländischen übersetzt von G. Siebert. 14 × 22 cm; pp. 482. Leipzig: Johann Ambrosius Barth, 1906. Price: paper, 8 marks; bound, 9 marks.*—The appearance of this text-book in one of the great culture languages is to be greeted with pleasure. We cannot have too many books of this sort, books that show how an able investigator handles the elements of his subject. The present volume is the first half of the text written by Lorentz for use in connection with his lectures on elementary physics, chiefly to students of medicine, at the University of Leiden. The mathematical methods employed are limited to elementary algebra; experimental methods, technical applications, and the history of the subject are left in the background; but everything presented is very simply, carefully, and clearly explained. In the arrangement of his material Lorentz exhibits the independence to be expected of him. In place of the usual separate discussions of mechanics, sound, light, heat, electricity, and magnetism, he distributes his matter in the very natural way indicated by

the headings—motion and forces, work and energy, rigid solid bodies, equilibrium and motion of fluids, properties of gases, thermodynamic considerations, properties of solid bodies, properties of liquids and vapors—which is as far as the present first volume goes. The whole is prefaced by a mathematical introduction, which is concerned with empirical and theoretical representation of measurements, graphs of algebraic and of periodic functions, surfaces, vectors, errors, derivatives, and maxima and minima. This is very satisfactory, and is distinctly an explanation of the ideas, rather than of the formal analysis, of elementary analytic geometry and differentiation. The book should prove extremely interesting and suggestive to teachers of the subject or of any part of it, and indeed to students who are able to read the German. The translation has been made with great care. *J. E. Trevor*

Die Fortschritte der kinetischen Gastheorie. *By G. Jäger. (Die Wissenschaft. Sammlung naturwissenschaftlicher und mathematischer Monographien. Heft 12). 14 × 22 cm; pp. ix + 121. Braunschweig: Friedrich Vieweg und Sohn, 1906. Price: paper, 3.50; linen, 4.10 marks.*—This little treatise on the kinetic theory of gases is divided into two equal parts, one giving an account of the older features of the theory, the other being an exposition of the more important developments of recent years. Limited space has caused the author to restrict himself to the theory of a gas consisting of perfectly elastic mutually attracting spheres. The introductory part of the volume presents the usual topics. The remainder is concerned with Boltzmann's H-theorem, the Maxwell-Boltzmann law, the characteristic equation for low compressions, the temperature coefficient of viscosity, temperature discontinuity in heat conduction, ideal liquids, the inner pressure of liquids, and the relation of the viscosity of ideal liquids to molecular dimensions. The excellence of the discussion is guaranteed by the author's name. The dedication is to Boltzmann. *J. E. Trevor*

La double Réfraction accidentelle dans les Liquides. *By G. de Metz. Scientia, No. 26. 13 × 20 cm; pp. 99. Paris: Gauthier-Villars, 1906. Price: paper, 2 francs.*—By accidental double refraction is here meant a double refraction temporarily brought about in a substance by the application of a mechanical, electric, magnetic, or other action. The aim of the present little book is to give as complete an account as possible of the existing state of knowledge of such double refraction in liquids. The author wishes hereby to attract the attention of experimentalists and theoreticians to this field of mechanico-optic, electro-optic, magneto-optic, etc., phenomena. Those interested in this difficult matter will doubtless be grateful to M. de Metz for providing them with this compact review of what has already been accomplished. *J. E. Trevor*

Lehrbuch der technischen Physik. *By Hans Lorenz. Zweiter Band: Technische Wärmelehre. 14 × 23 cm; pp. ix + 544. München and Berlin: R. Oldenbourg, 1904. Price: paper, 13 marks.*—The aim of this book, which appears as the second volume of Lorenz's *Lehrbuch der technischen Physik*, is stated to be to render available for further scientific and technical investigation the existing results of the study of thermal phenomena. To this end the author claims he has carried each of his chapters to the limits attained by the inquiry of the present time. The domain of the volume is a country of inter-

est to the physical chemist: the energy principle and the static behavior of perfect gases; phenomena of motion of perfect gases (sound, flow, resistance); the entropy principle and the behavior of saturated vapors; the behavior of imperfect gases or superheated vapors; chemical changes of state; motion of heat (conductivity, radiation); sketch of the historical development of the study of heat. The treatment of all this is interesting in many ways, but it seems to the reviewer that the interest attaches to the details of applications rather than to any excellence of the presentation of the general theory. The historical sketch is avowedly compiled from secondary sources.

J. E. Trevor

Kurzes Lehrbuch der organischen Chemie. *By A. Bernthsen. Neunte Auflage bearbeitet in Gemeinschaft mit Ernst Mohr. 14 × 21 cm; pp. xi + 637 Braunschweig: Friedrich Vieweg und Sohn, 1906. Price: paper, 11; bound, 11.80 marks.*—The new edition of the well-known "Bernthsen" has undergone considerable revision. The cyclical polymethylenes and the hexamethylene derivatives have been combined with the benzene derivatives to form a class of isocyclic compounds; and the heterocyclic compounds, formerly treated in part in the chapter on the "Transfer to the Aromatic Compounds" and in part with the benzene derivatives, have been assembled in a class by themselves. So the arrangement is no longer into methane derivatives and benzene derivatives, but into the three classes of methane compounds, isocyclic compounds, and heterocyclic compounds. These changes, together with extensive revision of the remaining text, dropping relatively unimportant matter and introducing important new matter, have been executed by Bernthsen's collaborator, Ernst Mohr.

J. E. Trevor.

Notions fondamentales de Chimie organique. *By Ch. Moureu. Deuxième édition, revue et augmentée. 14 × 23 cm; pp. 320. Paris: Gauthier-Villars, 1906. Price: paper, 7.50 francs.*—By the fundamental ideas of organic chemistry, M. Moureu understands an "exposition of the principal theories and a summary and very general study of the more important functions." He describes his book as an introduction to the study of organic chemistry, in which matters of detail or of secondary interest are not considered. Some judgment would have to be used in the employment of the book for the instruction of beginners; for the systematic part is prefaced by sixty-two pages of *théories générales*, for the grasp of which a considerable background of systematic organic chemistry must be presupposed. The systematic portions treat successively hydrocarbons, oxygen compounds, nitrogen compounds, metalloid-organic, metal-organic, and heterocyclic compounds. *J. E. Trevor*

REVIEWS

The object of this department of the Journal is to issue, as promptly as possible, critical digests of all Journal articles that bear upon any phase of Physical Chemistry.

Two-Component Systems

Alloys of nickel and antimony. *K. Lossew. Zeit. anorg. Chem.*, 49, 58 (*1906*).—From a determination of the freezing-point curve, the author deduces the existence of the two compounds NiSb and Ni_5Sb_2, for both of which maxima exist in the liquidus. NiSb does not form solid solutions with antimony, but at a temperature which is only 1° above that of the eutectic, NiSb is said to change into Ni_4Sb_5. The author was unable to prove this very satisfactorily, since the product of this transition forms a film around the still undecomposed NiSb, rendering equilibrium very difficult to obtain. He apparently did not try the very useful method of pouring the entirely melted alloy in drops into water and subsequently annealing this fine-grained structure to bring about the transition. The indications are, however, fairly satisfactory for the compound Ni_4Sb_5.

NiSb forms solid solutions with an excess of nickel. Ni_5Sb_2 does not form solid solutions with NiSb, but dissolves about 1 percent of Ni. Ni_5Sb_2 has an inversion temperature at 580°, and this inversion is detected only in the presence of an excess of Sb, and does not appear in the nickel-rich alloys containing more nickel than the composition of the compound. It is suggested that the inversion point may be dropped so rapidly by the 1 percent solid solution as to render its detection impossible. While this may be so, it seems a little hard to believe, and one would have preferred a little more evidence than the author has given as to the nature of the transition at 580°. Pure nickel dissolves about 8 percent of antimony in solid solution, and between the compounds Ni_5Sb_2 and the nickel solid solution, there is a range for mixtures of the compound and the solid solution. At 677° these mixtures of Ni_5Sb_2 and the solid solution combine with the formation of Ni_4Sb, as indicated by the heat change. This point was also checked microscopically, and it was found that the composition Ni_4Sb was homogeneous below 677°, and composed of two kinds of crystals above that temperature. There is a magnetic change in the solid solution at 330°, and strangely enough, the temperature of this change does not seem to be affected by the 8 percent of antimony dissolved in the nickel. There seems also to be a magnetic change at 90° in the mixtures of Ni_5Sb_2 and Ni_4Sb.

This paper is by far the most satisfactory which has come from this laboratory, being very conscientiously done. The author has discarded the interpolation formula used in previous papers for determining the probable freezing-point, has checked most of the transformations in the solid solution microscopically, and has used the annealing and quenching processes to some degree.

He has also dispensed with atomic percents, thereby greatly simplifying the diagram. While one would like to see some of the transformations a little more carefully investigated, the paper is on the whole a very satisfactory one, and the photographs accompanying it are excellent. *E. S. S.*

Alloys of magnesium with cadmium, zinc, bismuth and antimony. *G. Grube. Zeit. anorg. Chem.*, 49, 72 (*1906.*)—It will be remembered that Boudouard found a maximum in the magnesium-cadmium series for the composition MgCd. Grube finds that Boudouard's measurements are in error, as they have been in every case where his measurements have been repeated, and finds that, instead of a maximum, this series is a continuous series of solid solutions. He is, however, of the opinion that the compound MgCd exists and that it is this compound which forms solid solutions with the magnesium on the one hand and the cadmium on the other. At temperatures of 250° there is a distinct inversion in the composition MgCd and the concentrations to the right and left show this inversion falling away as it should.

Magnesium-Zinc.—The author finds a maximum corresponding to $MgZn_4$ is at about 51 percent of zinc and 345°. The compound melts at about 595°. The eutectic between the compound and pure zinc is at 368° and about 97 percent of zinc. He finds no reason to believe in the compound $ZnMg_4$ which Boudouard thought to be present.

Magnesium-Bismuth.—In this series there is a maximum for the compound Bi_2Mg_3 at a temperature of 715°. This compound forms a eutectic with pure magnesium at 550° and 65 percent bismuth. He was not able to determine any lowering of the freezing temperature of bismuth when magnesium is added, from which he concludes that the eutectic must contain practically none of the compound. The temperature is therefore 268°, that of bismuth. There is a perceptible evolution of heat when magnesium and bismuth combine to form this compound. It oxidizes in moist air and goes to pieces as a black oxide. The compound is stable in dry air.

Magnesium-Antimony.—This series shows a maximum at 961° at the composition Sb_2Mg_3. With pure antimony it forms a eutectic at 625° and at about 39 percent of antimony. It forms also a eutectic with antimony at 95 percent and 595°. There is no evidence of solid solutions in the work submitted. The compound renders the alloys extremely brittle.

The author has established the existence of the compounds CdMg, Zn_2Mg, Bi_2Mg_3, and Sb_2Mg_3. He has disproven the existence of $CdMg_4$, $CdMg_{30}$, and $ZnMg_4$ which Boudouard deduced from his very faulty experiments. He has also shown that the compounds MgCd, Bi_2Mg, Sb_2Mg_3 decompose water and are less stable in moist air than the pure components. On the other hand, the compounds Zn_2Mg and Al_3Mg_4 are less affected by water than by other components. *E. S. S.*

Silicides of nickel. *W. Guertler and G. Tammann. Zeit. anorg. Chem.*, 49, 93 (*1906*).—As a result of this investigation, the authors are led to predict the existence of 5 compounds, Ni_3Si, Ni_2Si, Ni_3Si_2, NiSi, and Ni_2Si_3. Nickel when hot will take up 5 percent of silicon as solid solution. This solid solution enters into a eutectic relation with Ni_3Si. At a temperature slightly below that of the eutectic the solid solutions react with the formation of Ni_3Si. Ni_3Si

forms solid solution with the Ni to about 8 percent. It also forms solid solutions with an excess of Si, which solid solution breaks down at lower temperatures to Ni_2Si and Ni_3Si_2. The evidence at this point is rather bad. However accurate the deduction may be as to the nature of the reaction, the line HI cannot have the significance which the authors attach to it. NiSi exists as a compound at a maximum, and apparently does not form solid solutions with the members on either side of it. The authors are not so certain about the compound Ni_2Si_3. The pyrometric evidence would seem to show that silicon retained quite a large portion of Ni in solid solution, but they do not state this to be true. It is shown that the hardness of the quenched alloys rich in nickel is less than that of the slowly cooled.

E. S. S.

The copper-cadmium alloys. *R. Sahmen. Zeit. anorg. Chem.*, 49, *301* (*1906*).—Of the very many different compounds of this series which have been predicted, the results of this investigation show only two, namely, Cu_3Cd_8 and Cu_2Cd. The former forms solid solutions to a certain extent with excess of Cu. The author undertook to produce the homogeneous Cu_2Cd by annealing the ingots, but as he allowed only three hours, there was not sufficient time for the reactions to occur, and was unable to produce it. In the reviewer's experience, a week's time is not too much to allow where reactions of this sort are to be brought about. It is also necessary to start with very finely crystallized material, a result which can readily be accomplished by pouring the molten alloy into water and annealing the shot thus produced. There is no reason to believe that copper forms solid solutions with cadmium nor cadmium with copper.

E. S. S.

Aluminum-bismuth and aluminum-tin alloys. *A. G. C. Gwyer. Zeit. anorg. Chem.*, 49, *311* (*1906*).—The author has redetermined the freezing-point for the aluminum-tin alloys, and finds that Anderson and Lean, as also Campbell and Mathews, were wrong in their experiments. There is no AlSn nor other compound in the series. The work confirms that done by Shepherd (8, 233 (1904)). Owing to the fact that the author did not allow any time for equilibrium to be reached, he finds the eutectic present throughout the series, and is led therefore to the opinion that there is no solid solution in the series. If he will take the trouble to anneal the alloys containing more than 85 percent of tin, he will find that the eutectic disappears. Aside from this error, due to the failure to recognize the importance of the time factor, the work is substantially a confirmation of the results published by Shepherd two years ago.

The aluminum-bismuth alloys give a case of practically complete immiscibility, thus giving two liquid layers for all compositions between the components. It is estimated that there may be perhaps 3 percent of bismuth dissolved in aluminum at the melting-point of the latter. No compounds occur, even when sufficient time is given, thus showing that the bismuth does not act like antimony in this respect.

E. S. S.

The equilibrium diagram for iron and sulphur. *W. Treitschke and G. Tammann. Zeit. anorg. Chem.* 49, *320* (*1906*).—The authors have done metallurgy a very great service in working out this quite difficult system, and their results seem to be well founded in experiment. Of the eight or more compounds be-

tween iron and sulphur which were supposed to exist, they find that between the ratio FeS and Fe there are no compounds whatsoever. In fact, the two components form a series of two liquid layers when fused. A certain amount of the sulphide is absorbed as solid solution by the γ- and β-varieties of iron. This amount is, however, rejected by the α-modification. There are two allotropic forms of FeS, the inversion temperature of which is 130°. FeS is able to hold a small amount of iron as solid solution and its melting-point is at about 1300°. Great difficulty was experienced with those melts rich in the sulphide because the compound attacks the porcelain of the pyrometer tube, destroying it in a very few minutes. This reaction is a very interesting one. The eutectic for FeS and Fe is at 16 percent Fe and 970°. In the presence of iron oxide this temperature may be lowered to 800°, thus materially affecting the properties of the iron in which the eutectic is present. *E. S. S.*

On the capacity of elements to form compounds with one another. *G. Tammann. Zeit. anorg. Chem.*, 49, *113* (*1906*).—The author tries to divide the elements into groups of similar nature as regards their ability to form compounds with one another. Unfortunately, the result is not successful, as our knowledge of the subject is entirely too limited. In some cases, where a series of solid solutions exists, the author considers that compounds exist, whereas a complete series of solid solutions is not regarded as combination. Recent work has shown that of the Cu-Sn alloys only one definite compound exists. The speculation, while interesting, is not sufficiently substantiated by the facts to warrant any great confidence at present. *E. S. S.*

Amalgamation of gold ores. *Thomas T. Read. Bulletin American Institute of Mining Engineers*, 1906, *467*.—This paper is a portion of a thesis which the author is preparing at Columbia University. It consists of a historical introduction in which the subject of amalgams in general is slightly touched upon, and then comes a short history of gold and silver amalgams. Under the heading "Research Work" the author found that the solubility of gold and mercury at 100° was very slight indeed, and he was unable to get any results from cooling curves. When we consider that even at 100° the quantity of gold still in solution is less than 1 percent and that the liquidus rises very rapidly, this failure to obtain results by the method of cooling curves is not surprising. The author then attacks the constitution of these amalgams by the thoroughly discredited method of trying to dissolve one of the phases chemically and leave the other intact. "It was inferred that if an alloy was prepared in which the gold was entirely in solution in the mercury and this alloy subjected to a solvent which would dissolve the mercury but not attack the solid phase, then we would get practically the effect of the freezing out of the solid phase by the removal of the mercury with which it was in equilibrium, finally leaving the solid phase present." Working in this way, always with an excess of gold present and with nitric acid as a solvent, the author comes out with two kinds of crystals which are apparently present together in the mercury and one of which he thinks is a solid solution containing about 13 atomic percents of mercury. Using different strengths of acid different results were obtained. In this case prismatic hexagonal crystals were obtained, and the author says that "their surfaces were bright and they had evidently not been attacked by the acid."

Le Chatelier made, the same mistake some years ago, but fortunately was able to correct it. The author finally concludes that not a great deal is to be learned in this way, and that it doesn't matter much anyhow, and goes on to the discussion of the silver amalgams with which he is even less successful than with the gold.

He next takes up the mechanics of the amalgamation process, and shows how a small particle of gold is caught by the layer of mercury on the plates. He offers some data on the rate at which mercury is absorbed by copper at different temperatures, and finds, as might be expected, that the absorption is much more rapid at 100 than at 0°. It is found that in time plain copper and silvered copper absorbed about the same amount of mercury, but the plain copper acts the more rapidly. Muntz metal is at first diminished in weight, due probably to the solution of the zinc, and then mercury is absorbed by the remaining composition. The amount of mercury absorbed by Muntz metal is scarcely one-fifth as great as that absorbed by plain copper for the same length of time. The author concludes, "since the Muntz metal is an inter-metallic compound of zinc and copper, there could be no possibility of any galvanic action between the zinc and copper to affect the process."

The author undertakes to determine the effect of temperature on the rate of amalgamation, and this he does by determining the angle at which balls of gold, silver and platinum will break away and run down amalgamated plates, first when the ball is at rest and second after the ball has been given a start. In this way, the author was unable to determine with certainty any very great difference between 0 and 100°.

The author has a hard problem, and he has not furnished a great deal of new and reliable information as the result of his experiments. It is to be hoped that he will repeat more carefully his investigations into the constitution of gold and silver amalgams, and clear up the question while he is at it.

E. S. S.

Multi-Component Systems

Experiments on the formation of quartz and silicates. *J. Königsberger and W. J. Müller. Centr. Min.*, 1906, *339*.—The authors, after mentioning the results obtained by van't Hoff in the investigation of the Stassfürt deposits, suggest that those minerals which are formed by deposition from solution can be investigated in a similar fashion. They have therefore undertaken to dissolve minerals in certain solutions under pressure and at high temperatures, filter the solution at the high temperature, and then allow the solution to remain for sometime at a lower temperature. Thereby, crystallization from the solution is obtained, and it is their purpose to find out what substances separate. It is doubtful if they appreciate fully the work of van't Hoff of which they speak. The solution which they take to be the proper one is that which is found in the liquid inclusions in quartz. This solution has the composition 85 percent of water, 5 CO_2, 2.5 Na, 1.5 K, Li, 0.3 Ca, 3.5 CO_3, 1.5 Cl, 0.7 SO_4. As is readily seen, the number of components becomes very uncertain under these conditions, especially when the mineral on which the solution is to act contains the additional components Al_2O_3, Fe_2O_3 and MgO.

Working in a platinum-lined tube so arranged that by inverting the tube the liquid in contact with the mineral being investigated was filtered through very fine sieves, they found that a certain glass was completely decomposed by water at 360° and gave good crystals of quartz along with certain other minerals which they were not able to identify. There was also a considerable portion of gelatinous silica present. The work will naturally be helpful in showing the attack on minerals in such solutions and the proximate solubility of the minerals in these solutions. It is to be hoped, however, that in the future they will choose simpler systems in order that the results may have some more definite value.

E. S. S.

Dielectricity and Optics

Experiments on the activity caused by uranium. *H. Becquerel. Comptes rendus*, 141, *87* (*1905*).—The radio-active matter in a solution of a uranium salt can be extracted with lampblack. The author tried the ingenious plan of burning the carbon in a platinum crucible. There was left behind a minute quantity of black grains which are strongly radio-active and which contain an oxide of uranium.

W. D. B.

The gases produced by actinium. *A. Debierne. Comptes rendus*, 141, *383* (*1905*).—A solution containing actinium bromide gives off hydrogen and oxygen gas, also traces of helium.

W. D. B.

Absorption spectrum of manganous salts. *P. Lambert. Comptes rendus*, 141, *357* (*1905*).—The author has mapped the visible spectrum of carefully purified manganous chloride. There is an absorption band extending from 557.50 to 513.00 and a second from 442.50 to 420. Between 412.25 and 394.50 there are no less than six narrow bands.

W. D. B.

Triboluminescence of metallic compounds. *D. Gernez. Comptes rendus*, 140, *1337* (*1905*).—Tschougaeff had found 121 organic compounds in 127 triboluminous substances and he drew the conclusion that triboluminescence is much more common in organic than inorganic compounds. The author gives a list of one hundred triboluminescent compounds, of which 74 are entirely inorganic while 26 are salts of organic acids.

W. D. B.

The reversibility of photographic development and the retarding action of soluble bromides. *S. E. Sheppard. Jour. Chem. Soc.*, 87, *1311* (*1905*).—The author has studied "the experimental attainment of an equilibrium in development" and "the influence of the chemical reactions in development on the velocity of the process." The reaction studied was that of a ferrous-ferric oxalate mixture on a silver bromide plate. The results obtained are in full accord with the "silver germ" theory proposed by Ostwald and Abegg and modified by K. Schaum.

W. D. B.

Photographic radiation of some mercury compounds. *R. de J. F. Struthers and J. E. Marsh. Jour. Chem. Soc.*, 87, *377* (*1905*).—Mercuric chloride is very active in sending out non-electrical radiations which affect a photographic plate. Mercuric cyanide does the same thing but to a much lesser extent. Mercuric bromide, mercurous nitrate and mercuric nitrate are all somewhat active while the other salts, so far as tested, are practically not active.

W. D. B.

ON THE RELATION OF CHEMICAL ACTIVITY TO ELECTROLYTIC CONDUCTIVITY.

BY JOHN LANGLEY SAMMIS

Introduction

The recognition of the fact that electrical and chemical phenomena may accompany each other under certain conditions, dates back to the time of Volta. Faraday demonstrated that the amount of chemical change effected and the amount of electric current which simultaneously passes through an electrolyte, bear a constant ratio to each other. From the vast majority of chemical changes known, we are at present unable to produce electricity directly; and it is equally true, that only in a very limited number of cases is it possible to effect chemical decomposition by direct application of the electric current. Nevertheless, since the time of Sir Humphry Davy, who originated the first electrochemical theory, there has been a lingering notion among chemists and physicists that all chemical action is essentially electrical in character. This idea has been rather vague and ill-defined; and it must be confessed that while it dominated in the dualistic system of Berzelius, it was forced into the background with that system by the development of organic chemistry. Of recent years through the rise of physical chemistry, the same notion has again come forward in somewhat modified form. The intensive study of the conductivity of electrolytes and of the rates with which chemical reactions proceed in homogeneous liquids that are capable of being decomposed by the direct agency of the electric current has led to the idea that chemical activity and electrolytic conductivity go hand in hand and are proportional to each other. In the language of the theory of electrolytic dissociation of Arrhenius, chemical action is supposed to take place between charged particles, or ions, which are considered as existing in the reacting bodies; and thus, since in a given case electrical conduction is supposed

to be proportional to the number of ions present, and the rate of chemical action would also be determined by the number of ions per unit of volume, the relation between electrical conductivity and chemical activity would be explained. It is unnecessary to dwell on this matter further, here, since it is fully set forth in the various books on the electrolytic dissociation theory and on physical chemistry which have appeared in recent years.

The question that naturally arises in considering whether there is an interdependence between chemical activity and electrolytic conductivity is twofold in nature. (1) In the case of a reaction which proceeds in a conducting liquid, is it possible to vary independently of each other within considerable limits the conductivity of the liquid and the rate of the chemical change? (2) Is it possible to produce all types of chemical reactions in liquids that are insulators as well as in liquids that are electrolytes? It is the purpose of this paper to take up the consideration of these questions from the experimental standpoint. While the first question raised has not hitherto been subjected to rigid direct test, a considerable amount of conclusive work has already been done on the second by Kahlenberg,[1] who showed that instantaneous chemical reactions, exactly like those that take place in solutions which are excellent electrolytes, may also go on in solutions that are the very best of insulators. So far as the second question is concerned, then, the work consisted of gathering experimental data in addition to those already collected by Kahlenberg; and in the course of this line of investigation it was found for the first time that it is indeed possible to replace one metal with another by direct action in insulating liquids, exactly as it is possible to accomplish this in conducting liquids. This discovery enables us to state that all reactions which take place in liquids that conduct the current may be reproduced as to type in liquids that are the best of insulators. In the study of the first

[1] "Instantaneous Chemical Reactions and the Theory of Electrolytic Dissociation," Jour. Phys. Chem., 6, 1 (1902).

question raised, the reactions whose rates were measured were the inversion of sugar, the catalysis of methyl acetate, and the solution of metallic magnesium in dilute acids. The acids used were nitric, hydrochloric and acetic. In order to reduce the conductivity after the first measurements had been made, similar solutions were prepared, in which an equal volume of benzol was substituted for part of the water present before, maintaining the percentages of acid and sugar or ester unchanged. While benzol is practically insoluble in aqueous sugar solutions, yet in the presence of sufficient acetic acid to invert the sugar at a rate convenient for measurement, a considerable proportion of the water can be replaced by benzol without causing two layers to form. The same end was reached in the other solutions, where nitric or hydrochloric acid was present instead of acetic, by using a mixture of water and acetone as a solvent. It was found in every case studied, that the substitution of benzol for part of the water, produced changes in the rate of chemical action and in conductivity which were entirely out of proportion to each other and not even always in the same direction.

Relation between Rate of Reaction and Electrolytic Conduction

(1) A solution (B) containing 29.4 grams of cane sugar in 57 cc of water at 25° C was mixed with 113.6 grams of glacial acetic acid, and the time of mixing was recorded. This solution was kept in a large Ostwald thermostat, containing a thermometer graduated to tenths of a degree, a thermoregulator and a stirrer. From time to time, the solution was examined in the polariscope, using an observation tube two decimeters long, surrounded by a water-jacket through which ran water at 25° C, during the observations. The instrument employed was of the Landolt-Lippich type made by Schmidt and Haensch and could be read by the vernier to 0.01 circular degree. The polariscope readings given below are each the average of six or more settings, and the time recorded is the number of minutes which had elapsed

from the time of mixing to the middle of the short period, during which the six successive settings were made. Shortly after the first polariscope observation was made, a portion of the solution was placed in a conductivity cell having circular platinized platinum electrodes about one centimeter apart and 2.5 centimeters in diameter and the conductivity was determined at 25° C. At the same time as the first, a second solution (A) was prepared, containing the same amount of sugar and glacial acetic acid as in (B), together with 36.2 cc water and 20 cc of benzol. The proportions in which these liquids are consolute have been determined by A. T. Lincoln.[1] The two solutions (A) and (B) were kept together in the thermostat, and examined alternately in the same polariscope tube, which was carefully washed and dried each time before use.

TABLE I

Solution (A)	Solution (B)
29.4 grams cane-sugar	29.4 grams cane-sugar
113.6 grams acetic acid	113.6 grams acetic acid
36.2 cc water	57.0 cc. water
20.0 cc benzol	—
Conductivity at 25° C	—
45.0×10^{-6}	218.0×10^{-6}

POLARISCOPE READINGS.

Time	Rotation	Time	Rotation
7 min.	19°.31	4 min.	18°.74
65 "	18.56	52 "	18.45
125 "	18.29	128 "	18.07
185 "	18.24	162 "	17.77
245 "	17.52	225 "	17.15
308 "	17.00	282 "	16.82
395 "	16.87	356 "	16.58
510 "	16.36	492 "	15.85
3510 "	12.04	3552 "	11.45
9600 "	3.66	9642 "	2.10

[1] Jour. Phys. Chem., 8, 248 (1904).

During the last two periods of time, the temperature of the thermostat varied somewhat, and the solutions, of course, underwent equal variations.

Change of rotation in		Change of rotation in	
510 min.	2°.95	492 min.	2°.89
3510 "	7°.27	3552 "	7°.29
9600 "	15°.65	9640 "	16°.64

The viscosity of these solutions at 25° C, was compared with that of water in a viscosimeter of the form described by Ostwald.[1] The specific gravity of solution (A) was 1.102, and

Time for water to flow out.....	2 min.,	13.7 sec.
Time for solution (A).....	10 "	47.2 "
Time for solution (B).....	10 "	2.2 "

that of solution (B) was 1.121 at 25° C. The small difference of viscosity in the solutions shows that this property is not to be held to account for the wide difference of electrical conductivity manifested by the solutions.

Ratio of the conductivities.....	4.8 to 1
Ratio of the rates of inversion.....	1 to 1

The use of benzol in solution (A) has reduced the conductivity in the ratio of 4.8 to 1, but did not materially affect the rate at which the inversion proceeded.

(2) In preliminary experiments with magnesium ribbon, it was found that several pieces cut from the same part of a strip, do not evolve hydrogen at a uniform rate when immersed in the same solution. In all the experiments with magnesium described below a cast bar of the metal was employed, which was found to act quite uniformly. This bar was 4.1 cm long and had a cross section of about 0.3 sq. cm. After cleaning the piece, it was dropped into an acid solution for ten minutes or so, while the hydrogen was being evolved and collected, then it was quickly removed, washed, and dried with filter paper, using care not to abrade the surface, and was ready for use in another solution. The effect of small changes of

[1] Hand- und Hülfsbuch, 1902, page 260, Fig. 168.

temperature upon the rate of such actions is marked.[1] The acids used were placed in bottles carrying thermometers graduated to tenths of a degree, and kept in a large thermostat also containing a thermometer, and cooled to 7° C. The magnesium was then dropped into the acid, a stop-watch was started, and the bottle was shaken steadily in the thermostat, as the action proceeded. The hydrogen evolved each minute was collected separately, so that any irregularities could be detected. Three acid solutions were prepared and the same bar of magnesium was dropped alternately into each. The experiments are numbered in the order in which they were performed.

Solution (A) was made of 68 cc glacial acetic acid and 32 cc of water. Its specific conductivity was 61×10^{-4}.

Solution (B) consisted of 68 cc of glacial acetic acid, 10.5 cc benzol and 20.5 cc of water. Its conductivity was 30×10^{-4}.

Solution (C) was composed of 34 cc of glacial acetic acid and 66 cc of water. Its specific conductivity was 76×10^{-4}.

During five minutes, the rise of temperature caused by the chemical action in the acid bottle was 1.5° to 2.0° in solutions (A) and (B), and about 5.0° in solution (C).

The use of benzol in solution (B) has decreased its conductivity to less than one-half that of (A), yet its action upon the metal has been diminished by only about 20 percent.

Comparing solutions (A) and (C), it is apparent that the use of more water in (C) has increased the chemical activity of that liquid toward magnesium to about 625 percent of that of (A), while at the same time the specific conductivity has been increased by only 25 percent. If the same solutions had not been used, but fresh ones prepared, the differences between 6, 7 and 9 would disappear, and further emphasize the conclusions drawn.

(3) Another experiment, similar to the last, was performed, using different acid solutions. Solution (A) consisted

[1] Cf. Spring: Bull. Soc. Chim., Paris (3), 3, 181 (1890).

of 50 cc of glacial acetic acid and 50 cc of water. Solution (B) was composed of 50 cc glacial acetic acid, 25 cc acetone, and 25 cc of water. The same bar of magnesium was used as before.

TABLE II

VOLUME OF HYDROGEN EVOLVED BY ONE AND THE SAME BAR OF MAGNESIUM FROM

Time	Solution (A) Experiment No.			Solution (B) Experiment No.			Solution (C) Experiment No.		
	2 cc	4 cc	8 cc	1 cc	3 cc	5 cc	6 cc	7 cc	9 cc
0.5 min.	—	—	—	—	—	—	16.5	12.0	12.0
1.0	5.0	4.75	4.2	4.2	4.0	3.8	17.5	13.0	11.75
1.5	—	—	—	—	—	—	17.0	14.0	12.0
2.0	4.5	5.1	4.0	4.0	3.75	3.5	17.5	14.5	12.5
2.5	—	—	—	—	—	—	17.5	14.8	12.5
3.0	5.0	4.75	4.5	4.0	3.5	3.5	17.7	14.5	13.0
3.5	—	—	—	—	—	—	18.2	15.0	13.0
4.0	5.0	5.0	4.25	3.9	3.75	3.5	18.2	15.0	13.5
4.5	—	—	—	—	—	—	18.0	15.0	13.0
5.0	5.5	5.1	4.75	4.0	4.36	3.4	19.2	15.0	13.5
Average cc. per minute	4.76			3.89			29.7		
Specific conductivity	61.0×10.0^{-4}			30.0×10^{-4}			76.0×10^{-4}		

TABLE III

VOLUME OF HYDROGEN EVOLVED BY BAR OF MAGNESIUM FROM

Time	Solution (A) cc	Solution (B) cc
0.5 min.	13.0	6.0
1.0	14.0	6.5
1.5	14.0	6.25
2.0	14.5	6.5
2.5	14.5	6.5
3.0	15.0	—
3.5	15.5	11.75
4.0	15.5	—
4.5	15.5	11.75

The total volumes of hydrogen are 131.5 cc from solution (A) and 55.2 cc from solution (B), the ratio being 2.38 to 1.

The electrical conductivity of solution (A) was 931×10^{-6}; and that of solution (B) was 158×10^{-6}, the ratio being 5.9 to 1. If the conductivity is any measure of the number of ions, which are supposed to produce the chemical activity, it is difficult to see how the activity of the liquid can increase so much faster than the conductivity.

(4) Another experiment of this sort will be described. Solution (A) containing 50 cc of glacial acetic acid and 50 cc of water, and its conductivity at 7.5° C was 69×10^{-6}. Solution (B) consisted of 4 cc of 5N hydrochloric acid, 76 cc of acetone, and 22.5 cc of benzol. Its conductivity was 70×10^{-6}.

TABLE IV

VOLUME OF HYDROGEN EVOLVED BY BAR OF MAGNESIUM FROM

Time	Solution (A) cc	Solution (B) cc
30 seconds	10.75	—
60	12.25	6.0
90	12.25	—
120	12.5	6.1
150	11.0	—
180	13.75	5.75
210	12.5	—
240	13.0	5.9
270	13.0	—
300	13.0	6.2
	124.0	29.95

The ratio of the rates of hydrogen evolution is 4.1 to 1.0, whereas the conductivity of the solutions is practically identical.

(5) A solution of 10 cc lactic acid, 65 cc of water, and 42 cc of acetone was observed to evolve hydrogen at the rate of 1.4 cc per minute, when the bar of magnesium was dropped into it. The conductivity of the solution was 71×10^{-6} at 25° C. Another solution containing 3.33 cc of the same lactic acid, 60.67 cc of water, and 30 cc of acetone, evolved hydrogen at the rate of 1.07 cc per minute, and its conductivity was 74×10^{-6} at 25° C. Here the activity is increased and the

conductivity is diminished at the same time and by the same means.

In all of these experiments, it was carefully noted that the metal at no time became coated with anything like a scale or crust during the action of the acids upon it. On the contrary, it shone with a silvery lustre undimmed at any time. The products of the action were in every case completely soluble in the liquids. The gas evolved did not adhere to the metal, but escaped rapidly from its surface. The solution, being continually shaken, remained uniform in composition and the rate of action was not affected by the accumulation of the products in any one portion of the solution.

(6) Another favorite method of determining the activity of acids is to observe the rate at which they cause the catalytic decomposition of esters. Ostwald has recorded experiments showing how the addition of acetone to a nitric acid solution affects the rate at which it decomposes methyl acetate. He did not, however, record any conductivity measurements on these solutions. The following table is copied from his published results.[1] In each of the six mixtures there was present 5 cc 2N nitric acid, 2 cc methyl acetate, and other substances as indicated below.

TABLE V

Solution No.	Solvent	Ester decomposed in four hours
(1)	8 cc water, 0 cc acetone	23.14 cc standard baryta
(2)	7 cc " 1 cc "	21.91 cc "
(3)	6 cc " 2 cc "	21.56 cc "
(4)	4 cc " 4 cc "	17.83 cc "
(5)	2 cc " 6 cc "	15.11 cc "
(6)	0 cc " 8 cc "	12.00 cc "

For the purpose of this study, solutions were prepared having exactly the same composition as those listed above and their conductivity was determined, the results being as follows:

[1] Jour. prakt. Chem. 136, 460 (1883).

TABLE VI

Solution No.	Specific conductivity
(1)	26.5×10^{-3}
(2)	25.6×10^{-3}
(3)	25.2×10^{-3}
(4)	19.5×10^{-3}
(5)	13.6×10^{-3}
(6)	8.1×10^{-3}.

It is clear that by the use of acetone the electrical conductivity is diminished about 1.7 times faster than the chemical activity with respect to the catalysis of the ester.

(7) The preceding experiments have served to indicate that by the use of suitable solvents the electrical conductivity of a solution can be varied very greatly without at the same time effecting a corresponding change in the chemical activity. To test this view still further, the following experiment was performed. Three solutions were prepared.

TABLE VII

Solution (A)	Solution (B)	Solution (C)
5 cc 5N HCl 60 cc water —	5 cc 5N HCl 12.5 cc acetone 47.5 cc benzol	5 cc 5N HCl — 60 cc acetone

The specific conductivity of these solutions was respectively, 39000×10^{-5}, 171×10^{-5}, 365×10^{-5}.

After adding 10 cc of methyl acetate to each, the conductivity was 26480×10^{-5}, 215×10^{-5}, 312×10^{-5}.

The rate at which the ester was decomposed was determined by titrating portions of the liquids with standard baryta solution, at intervals, as indicated in the table.

Comparing the aqueous acid (A) with the acetone acid (C), it is clear that the former conducts about 107 times as well as the latter, but decomposes methyl acetate only about 1.6 times faster. Similarly, solution (A) has about 228 times the conductivity of (B), yet it decomposes methyl acetate

Time Minutes	cc	Time Minutes	cc	Time Minutes	cc
10	2.3	7	1.25	8	1.8
16	2.7	12	1.85	15	2.1
58	4.35	22	2.10	63	3.25
142	7.50	93	3.60	144	5.85
206	9.60	198	6.10	206	6.75
274	11.60	265	6.80	277	7.80
324	13.00	324	7.65	326	8.15
357	13.75	376	8.10	374	8.55
		444	8.75		

only about 2.6 times as fast as (B). It is evident that here no interdependence exists between the conductivity of these acids and the rate at which they decompose the ester, and it is equally certain that by the selection of suitable solvents the conductivity can be varied at will and practically independently of the activity. The following table contains a summary of the preceding experiments.

TABLE VIII

Experiment	Rate of activities	Rate of conductivities
(1) Sugar inversion.....	1 : 1	1 : 4.8
(2) 68 percent acids-magnesium.....	1 : 1.2	1 : 2.0
(3) 68, 34 percent acids-magnesium.....	1 : 6.25	1 : 1.25
(4) Acetic acid, HCl, and magnesium....	1 : 4.1	1 : 1
(5) Lactic acid and magnesium..... ..	1 : 1.31	1 : 0.96
(6) Methyl acetate and nitric acid.....	1 : 1.92	1 : 3.27
(7) Methyl acetate and hydrochloric acid	1 : 6.0	1 : 107
(8) Methyl acetate and hydrochloric acid	1 : 7	1 : 228

It may be noted here that in 1, 2, 6, 7, 8, above, the conductivities change more rapidly than the rate of chemical activity, while in 3 and 4, the activity changes more rapidly than the conductivity. In 5, is found a case of simultaneous decrease of conductivity and increase of activity. There would be no difficulty in multiplying such cases *ad libitum*. The discussion of these results will be undertaken later.

Chemical Activity in Non-Conducting Solutions

Previous studies at this University have shown that certain chemical reactions do take place with ease in non-conducting solutions. Kahlenberg[1] has shown that the oleate of cobalt dissolves in toluene to a red solution which turns blue on heating, and red again on cooling. Zinc is attacked by a benzene solution of hydrochloric acid gas. Tin, aluminum, lead and sodium also react like zinc but less vigorously. The solution of hydrogen chloride in benzene precipitates brown cupric chloride from copper oleate solution, brownish yellow nickel chloride from nickel oleate solution, and blue cobalt chloride from cobalt oleate solution in benzene. Tin tetrachloride, phosphorus trichloride, arsenic chloride, and silicon tetrachloride behave like hydrochloric acid in precipitating these insoluble chlorides from the non-conducting solutions. Dry hydrogen sulphide passed into the benzene solutions of the oleates of copper, nickel, or cobalt or the chlorides of tin or arsenic precipitates the sulphides of these metals. In benzene solution, dry ammonia and dry hydrogen chloride combine and precipitate solid ammonium chloride. Dry pyridine in benzene solution forms with dry hydrogen chloride the white crystalline pyridine hydrochloride at once. None of the above-mentioned solutions conduct the current. Working in this laboratory, J. H. Mathews[2] found that trichloracetic acid dissolves in ethyl silicate to a solution having a specific conductivity less than 3×10^{-8}, which attacks magnesium rapidly with evolution of hydrogen. A saturated solution of trichloracetic acid in nitrobenzene exhibits a specific conductivity of 1.46×10^{-6} and acts upon zinc, nickel, magnesium, cobalt, cadmium, copper, bismuth, iron and sodium with various degrees of vigor. Trichloracetic acid in benzene acts on the metals vigorously but its conductivity is less than 3.8×10^{-8}. The same result is obtained with a kerosene solution of trichloracetic acid.

[1] Jour. Phys. Chem., 6, 6 (1902).
[2] Ibid., 9, 641 (1905).

Magnesium acts upon the non-conducting solutions of crotonic, trichlorlactic, glacial acetic and dichloracetic acids. A 41 percent solution of cyanogen iodide in allyl mustard oil shows a conductivity of 1.36×10^{-9} and attacks magnesium, sodium and zinc. Kahlenberg[1] observed that normal solutions of trichloracetic acid in methyl, ethyl, or amyl sulphocyanates or in ethyl or allyl mustard oils rapidly attack magnesium and the dry carbonates of sodium and potassium, while the solutions are excellent insulators. Kahlenberg and Schlundt[2] have observed that liquid hydrocyanic acid, whose specific conductivity was 0.4×10^{-6}, attacks sodium and potassium, but fails to attack other metals or carbonates. Solutions of hydrogen chloride and other acids in liquid hydrocyanic acid conduct much better, but fail to attack various metals and carbonates.

Continuing this line of work under Professor Kahlenberg's direction, I have found that the precipitation of one metal by another from a salt solution takes place in non-conducting solutions also. For the purpose of these experiments, solvents were selected which do not themselves conduct the current, such as benzol, kerosene, pyridine and a great variety of other organic liquids. The ordinary salts of the metals, as the chlorides, acetates, sulphates, or nitrates, are quite insoluble in most of these liquids; but certain of the salts of organic acids, as the oleates and palmitates, are easily soluble in many of them. In general, these solutions conduct no better than the solvents themselves. Where the solvent is observed to show some slight conductivity of its own, the addition of copper oleate or other soluble copper salt to the liquid is quite as likely to decrease as to increase the conductivity. For example, a sample of amyl nitrite from Schuchardt showed a conductivity of 1.5×10^{-6}, and after dissolving a few percents of copper oleate in it, the conductivity was found to be 1.1×10^{-6}. The conductivity of a specimen of turpentine which had been dried by calcium chloride was

[1] Zeit. phys. Chem., 46, 63 (1903).
[2] Jour. Phys. Chem., 6, 447 (1902).

found to be less than 1.6×10^{-8}, and after dissolving some copper oleate in it, the conductivity was found to be practically unchanged. It was next sought to determine whether such solutions as these act chemically upon the metals. Only a small portion of this field could be explored even in a qualitative way, as the total number of possible reactions is very great.

Action of Metals on Copper Oleate Solutions

A solution of copper oleate in amyl nitrate was found to have a conductivity of 2.6×10^{-7}, the same as the pure solvent. This was placed in a flask with pieces of copper, silver, bismuth, cadmium, antimony, magnesium, cobalt, aluminum, tin, iron, lead and solder, connected to a reflux condenser, carrying a calcium chloride tube at its upper end, and heated in a boiling water bath for two hours. The lead and cadmium were found to be coated with bright red metallic copper, the bismuth was tarnished somewhat and all the rest of the metals were unaffected. The metals used in these tests were of the best quality obtainable, and were all scraped bright with a steel tool before use, each time. The copper oleate was pure and anhydrous, as was also the amyl nitrate.

A solution of copper oleate in kerosene was heated 3.5 hours to 100° C with zinc, solder, lead, silver, cobalt, nickel, copper, bismuth, antimony, magnesium, tin, platinum, cadmium and iron. The zinc, cadmium and lead were found to be coated with metallic copper, and the other metals were unaffected. The lead acted most rapidly. Sodium was not affected by heating to 100° C under the solution of copper oleate in kerosene.

Using carbon bisulphide as a solvent for the copper oleate, magnesium, platinum, iron, antimony, bismuth, cobalt, nickel, solder, silver, tin and lead were all unaffected by heating the solution to boiling for four hours. No copper was deposited in any case. In a sealed tube, the carbon bisulphide solution was heated with zinc, aluminum, cadmium, silver, magnesium, tin, cobalt, nickel, iron, antimony, bismuth,

manganese, lead, and solder to 100° C for two hours, and then left in the cold thirty-six hours longer. The silver was observed to be blackened. The solution was still blue, and no red metallic copper was deposited in any case.

A solution of copper oleate in ethyl acetate, dried by calcium chloride, was heated to boiling for three hours with bismuth and cadmium which were slightly tarnished thereby, and with iron, tin, silver, zinc, solder, magnesium, antimony and aluminum which were not changed. Metallic lead was not affected by boiling five minutes in this solution. The conductivity of the solution was less than 1.6×10^{-8}.

In dry acetone solution of copper oleate, heated to boiling for three hours, magnesium, cadmium, tin, platinum, nickel, copper, zinc, aluminum, antimony, bismuth and iron remained unchanged. The conductivity of the solution was 2.6×10^{-8}.

In a sealed tube, a solution of copper oleate in carbon tetrachloride was heated to 100° C for two hours. The zinc and lead had each a little dark red powdery deposit on them, and the other metals remained perfectly bright and unattacked.

In benzylamine solution of copper oleate, heated to 100° C for four hours, zinc and cadmium were coated with a slight pulverulent deposit, lead received a bright red deposit of metallic copper, while silver, magnesium, bismuth, antimony, zinc, cadmium, tin, nickel, cobalt, platinum, iron and aluminum remained perfectly bright and unchanged.

A solution of copper oleate in pyridine was heated to its boiling-point for two hours in a paraffin bath with zinc, cadmium, silver, lead, magnesium, platinum, iron, bismuth, antimony, tin, solder, nickel, and cobalt. The lead and cadmium were found to be coated with copper and the zinc was tarnished. The other metals were unchanged. Thallium was tarnished in the same liquid on warming. The pyridine used was of "medicinal" purity from Merck. It was dried with caustic potash and redistilled before use. It boiled at 113.5–116.5° C, uncorrected. The conductivity of the pyridine was less than 1.6×10^{-8}.

Replacement of Copper by Lead in Non-Conducting Solution

After digesting a solution of copper oleate in pyridine in a flask with a strip of lead for two hours at the boiling-point, under the reflux condenser, the liquid was of a brown color and no green or blue was visible. The lead was thickly coated with a layer of coherent copper, bright red, and lustrous, which flaked off in large pieces on rubbing. It was washed in alcohol and ether and preserved. The liquid was filtered and evaporated to free it from pyridine, the residue was dissolved in alcohol and dilute nitric acid, heated and treated with hydrogen sulphide. The black precipitate of sulphide was filtered, washed, and dissolved in nitric acid, evaporated with C. P. sulphuric acid and diluted with alcohol. The heavy white precipitate of lead sulphate obtained was washed, dried, and preserved. On evaporating the filtrate to small bulk, and adding ammonia, a faint blue color showed the presence of a small amount of copper in the solution. It is hereby shown that lead actually dissolves at the same time the copper is precipitated, and that the reaction which takes place when lead acts on a copper oleate solution in pyridine may be expressed by the equation

$$(C_{18}H_{33}O_2)_2Cu + Pb = (C_{18}H_{33}O_2)_2Pb + Cu.$$

Influence of Water on Action of Lead on Copper Oleate

In order to see what influence the presence of small proportions of water would have, portions of the copper oleate pyridine solution were heated in test-tubes with various metals to 100° C, then 10 percent water was added slowly, continuing the heating. In the tubes containing iron, tin, antimony, bismuth, cobalt, aluminum and silver no change whatever occurred on adding water. In the tubes containing magnesium, cadmium, and zinc, the addition of water caused a distinct red metallic deposit of copper. In the tube containing calcium both hydrogen and copper were deposited on adding water.

Using toluene as the solvent for the copper oleate, it was observed that lead precipitates metallic copper upon

standing a few hours in the cold, or at once, if the solution be heated, while magnesium, zinc, silver, bismuth, tin, solder, cadmium, iron, antimony, cobalt, nickel, platinum, manganese, mercury, aluminum are unaffected in any way at 100° C in six hours. Sodium melted under the toluene solution of copper oleate is not changed. The conductivity of the solution is less than 1.8×10^{-8}. The oleates of cadmium, magnesium, zinc, manganese, nickel, iron and cobalt are all easily and completely soluble in toluene. Some of the toluene was treated with phosphorus pentoxide in a distilling flask, and after several days was distilled into a dry flask containing metallic lead and dry copper oleate. The apparatus was put together air-tight, and the flask was protected by a calcium chloride tube passing through the cork. Without disconnecting the receiver, the distillate was gently warmed by a lamp, when the copper oleate dissolved rapidly, and the metallic copper precipitated abundantly at once. These experiments show that the presence or absence of water in small proportions does not determine the precipitation of copper by lead in these cases.[1] In order to see whether other oleates behave like copper oleate, the following experiments were performed.

Action of Metals upon Various Other Metallic Oleates

Small portions of the oleates of manganese, chromium, nickel, cobalt, iron, and cadmium, were dried at 150–175° C for two hours and cooled in a desiccator. The solution of the dried nickel oleate in toluene was boiled with pieces of metallic magnesium, cadmium, zinc, bismuth, antimony, lead, tin, cobalt, aluminum, silver, manganese, platinum, iron, solder and copper for two hours under a reflux condenser, provided with a calcium chloride tube at the upper end. None of these metals was affected, excepting lead, which was covered with a black scale.

Manganese oleate in toluene solution, was heated similarly

[1] In this connection compare the work of J. H. Mathews upon the effect of small amounts of water. Jour. Phys. Chem., 9, 641 (1905).

with lead, magnesium, zinc, antimony, silver, cadmium, iron, cobalt, aluminum, bismuth, solder, nickel, and copper. The only metal affected in any way was lead, which was covered with a black scale.

Cobalt oleate solution in toluene was placed in a flask with metallic silver, magnesium, cobalt, antimony, lead, tin, zinc, manganese, bismuth, copper, cadmium, iron, platinum and nickel and heated to boiling for two hours. The only metals changed were lead which received a black deposit, and copper which was stained nearly white, with a metallic lustre.

Chromium oleate in toluene was heated with metallic silver, magnesium, cobalt, antimony, lead, tin, iron, zinc, nickel, cadmium, bismuth, copper and manganese; but as before, lead alone was affected and this was coated with a black scale.

Ferrous oleate in boiling toluene solution, for two hours, with bismuth, antimony, nickel, iron, zinc, cadmium, magnesium, tin, silver, aluminum, cobalt, copper, lead and manganese, did not affect any of these metals.

Cadmium oleate in boiling toluene solution, for two hours with cobalt, cadmium, bismuth, antimony, silver, copper, magnesium, lead, zinc, iron, tin, aluminum and nickel, deposited a fragile black scale on the lead, and all of the other metals were unaffected. The solution gelatinized on cooling.

The experiments described above indicate that the reaction of lead with the copper oleate solutions proceeds far more rapidly and easily than any of the others tried, and the study of this reaction was therefore taken up in greater detail. The black scales observed in a few cases above, which formed also on lead in a few copper solutions, as noted below, were always very small in amount. They were too thin and minute in quantity to separate from the lead for analysis; and consequently, they were not examined further than to test some of them for radioactivity, which property was, however, not observed in any case. The question now arose as to whether other salts of copper behave toward lead like the oleate.

Action of Metals on Copper Salts Other than the Oleate

Copper palmitate was prepared by adding to copper sulphate, in aqueous solution, an equivalent quantity of solution of potassium palmitate, which was prepared by treating pure palmitic acid with the requisite quantity of potassium hydroxide. The precipitate was washed free of sulphate by decantation, and dried at 100° C to a fine blue powder. The salt melts at higher temperatures without apparent decomposition. A toluene solution of this salt was heated to boiling for two hours with bismuth, magnesium, antimony, cobalt, silver, zinc, lead, tin and cadmium. The lead was thickly coated with black scale, the bismuth was tarnished, and the others were entirely unchanged.

Copper palmitate dissolved in pyridine deposits bright red metallic copper on lead at once on gently warming.

A sample of abietic acid prepared from Oregon balsam, furnished by Professor Kremers, was made into the copper salt, which was dried at 120° C. The boiling pyridine solution of this salt did not act on lead.

Capronic acid (ex butyric acid) was redistilled, boiling-point 196–199° C, and converted into the copper salt by neutralizing with caustic potash and then adding copper sulphate solution in molecular proportion. The copper capronate was washed by decantation till entirely free from sulphate, and dried in air to a fine blue powder. On heating up the blue salt to about 100–125° C, it suddenly turned green and remained green on cooling. The change in color took place suddenly and uniformly throughout the mass. Both the blue and green varieties dissolve easily in pyridine to a green solution. On heating this solution with lead, the liquid turns brown instantly, and deposits copper on the lead at once, from the fairly strong, hot solution, but not so quickly if the solution is more dilute.

Crystallized copper acetate, from Schuchardt, was found to dissolve in pyridine to a deep blue solution whose conductivity was 6.6×10^{-7}. The solution was quite dilute. Metallic lead gently warmed in this solution was quickly coated with a bright red precipitate.

Crystallized copper formate from Schuchardt, dissolved in pyridine to a deep blue solution, whose conductivity was 9.6×10^{-7}. This quite dilute solution heated with lead turned green and deposited copper on the lead at once.

It is thus perfectly clear that the action of lead on copper salts is not restricted to the oleate, since the capronate and palmitate act in the same way.

Action of Lead on Fused Copper Salts

To test the action of lead upon the copper salts in the absence of solvents, the salts were placed in test-tubes and heated in a paraffin bath which contained a thermometer and a stirrer. As soon as each salt melted, a piece of lead was dropped into it and the temperature was held constant for a few minutes. The lead was then withdrawn with its adhering layer of fused salt, and after cooling in air, was dipped into some carbon bisulphide, which rapidly dissolved off the copper salt and exposed the clear surface of the metal. Carbon bisulphide was used because it had already been shown that solutions of copper oleate in this solvent do not attack lead. By this method, it was found that fused oleate deposits copper on lead at 100° C in five minutes or less.

Copper palmitate has a higher melting-point. At 125–140° C, it was quite fluid and deposited copper on the lead easily.

Copper abietate at 185–195° C, did not deposit copper on lead. Clean lead pressed into copper oleate somewhat softened by warming was found to have precipitated no copper at all in twelve hours.

Do Solvents Aid or Hinder the Action of Lead on Copper Oleate?

In order to find out whether various solvents aid or prevent this reaction between lead and copper oleate, these solvents were first examined as to their conducting power, then the liquid in the conductivity vessel was poured out into a clean testtube, a fragment of copper oleate was added and the liquid warmed, but not above 110–115° C. If copper was

deposited on the lead in the tube, the liquid was poured back into the conductivity cell, in order to determine the conductivity of the solution. In the following tables, the word "none" means that no conductivity could be detected by means of the telephone, Wheatstone's bridge, and 11000 ohms resistance, according to the method of Kohlrausch. In such cases, the conductivity, if any, is less than 1.6×10^{-8}. Lead precipitates copper from a solution of copper oleate in each solvent in the following list.

TABLE IX

Solvent	Spec. cond. of solvent	Spec. cond. of solution
Kerosene	None	None
Nonane (Ohio petroleum)	None	"
Petroleum (Japanese) B. P. 116–118	Not determined	—
" " " 196–197	" "	—
Amylene	" "	—
Dipentene (S)	" "	—
Paraffin, melted	" "	—
Diphenylmethane (K)	" "	—
Triphenylmethane, melted (K)	" "	—
Toluene (S)	None	None
Xylol	Not determined	—
Spermaceti, melted (E)	" "	—
Limonene	None	None
Retene, melted (S)	Not determined	—
Turpentine	None	None
Cymene (*e*-camphora)	Not determined	—
Terpinene	None	None
Mesitylene	Not determined	—
Naphthalene, melted	" "	—
Anthracene, melted (M)	" "	—
Alcohols and Phenols		
Ethyl, by CaO (S)	2.2×10^{-6}	9.0×10^{-6}
Isopropyl (S)	3.3×10^{-6}	5.6×10^{-6}
Normal propyl (S)	7.4×10^{-7}	1.5×10^{-6}
Allyl	Not determined	—
Isobutyl	3.4×10^{-7}	None
Isoamyl (K)	5.1×10^{-7}	5.1×10^{-7}
Cumol	—	—
Guaiacol (Merck)	2.6×10^{-7}	2.0×10^{-7}
Eugenol (S)	None	None
Phenetol (S)	"	"

TABLE IX—(*Continued*)

Solvent	Spec. cond. of solvent	Spec. cond. of solution
Alcohols and Phenols		
Phenol, white, melted (K)	None	4.7×10^{-7}
Thymol, melted (S)	Not determined	—
Meta-kresol (S)	None	None
Ortho-kresol methyl ether (S)	"	"
Terpineol (S)	"	"
Carvacrol	Not determined	—
Amines, etc.		
Pyridine	None	None
Dibenzylamine	"	"
Benzylamine	"	"
Aniline	"	0.2×10^{-7}
Picoline (S)	5.3×10^{-7}	8.1×10^{-7}
Ortho-toluidine (M)	1.7×10^{-6}	1.7×10^{-7}
Quinoline, synthetic, redistilled (S)	None	None
Urethane, melted (S)	Not determined	"
Pyrrol	" "	"
Ethereal Salts, etc.		
Ethyl oxalate	1.1×10^{-6}	9.6×10^{-7}
Ethyl carbonate	None	None
Ethyl nitrate	2.0×10^{-6}	6.7×10^{-7}
Amyl nitrate (S)	2.6×10^{-7}	2.6×10^{-7}
Amyl nitrite (S)	1.5×10^{-6}	1.1×10^{-6}
Amyl benzoate (S)	None	None
Amyl acetate	Not determined	—
Aceto-acetic ester (S)	1.7×10^{-6}	Not determined
Monochlorhydrin (S)	4.9×10^{-7}	8.7×10^{-6}
Dichlorhydrin (S)	1.09×10^{-5}	7.38×10^{-6}
Cottonseed oil, refined	Not determined	—
Brombenzene	None	None
Benzyl aceto-acetate (S)	Not determined	—
Nitriles, etc.		
Capro-nitrile	3.3×10^{-6}	3.2×10^{-6}
Valero-nitrile (S)	5.4×10^{-6}	4.2×10^{-5}
Benzo-nitrile	9.9×10^{-6}	3.1×10^{-6}
Toluo-nitrile	5.4×10^{-6}	4.2×10^{-5}
Nitrobenzene (K)	4.0×10^{-7}	4.0×10^{-7}
Aldehydes, ketones, etc.		
Acetyl-acetone (S)	3.6×10^{-6}	4.2×10^{-6}
Acetyl methyl hexyl ketone (S)	None	None
Acetophenone	1.6×10^{-6}	2.2×10^{-6}
Anisic aldehyde (S)	1.7×10^{-6}	1.7×10^{-6}
Benzaldehyde (not free of acid)	Not determined	—
Menthone	None	None

Solutions of copper oleate in the following solvents gave no deposit of copper on lead, even after heating above the boiling-point of the solvent in a sealed tube. The solutions were, however, quite dilute and it is possible that stronger solutions might act in some cases.

TABLE X

Solvent	Spec. cond. of solvent	Spec. cond. of solution
Acetone	2.6×10^{-6}	Not determined
Methyl sulphate	1.9×10^{-4}	2.0×10^{-4}
Methyl iodide (K)	1.3×10^{-7}	None
Ethyl acetate	None	"
Ethylidene chloride (S)	"	1.3×10^{-7}
Pentane (S)	Not determined	—
Hexane (S)	" "	—
Ligroin	" "	—
Rhigolene	" "	—
Benzol, thiophene-free	" "	—
Furfurol (S)	6.8×10^{-6}	7.8×10^{-6}
Carbon bisulphide	Not determined	—
Carbon tetrachloride	"	—
Piperidine (S)	"	—

The letters in parentheses (S), (K), (M), (E) indicate the source of the substance, Schuchardt, Kahlbaum, Merck, Eimer and Amend. All of the copper oleate used was dried in an air-bath at 130°–140° C in thin layers before use and was afterward cooled over sulphuric acid in a desiccator and preserved in stoppered weighing-tubes. The other copper salts were similarly dried and none of them show any indication of being hygroscopic. The solvents were anhydrous and of the best grade, and some of them were especially dried with great care.

The experiments already described show that the solvent, the metal, the acid radical in the copper salt, and the temperature are all important factors in determining whether reaction occurs or not. It was observed also that stronger solutions of copper oleate in pyridine or toluene act more rapidly on lead than dilute solutions, and this fact led to an

attempt to compare these rates of action. A preliminary experiment was begun in which the rates of deposition of copper from solutions of different concentration were to be estimated from the rate at which the blue color disappeared from the liquids. The colorimetric measurements were, however, not performed, on account of the appearance of new and unforeseen phenomena, to be described below.

Effect of Concentration on the Precipitation of Copper by Lead from Copper Oleate Solutions

Two grams of copper oleate were weighed in a flask and 38 grams of pyridine were added, making a 5 percent solution of the salt. This was placed in a burette and diluted in test-tubes with pyridine from another burette, as follows, thus preparing solutions with approximately the percentage composition indicated.

n cc 5 percent sol. of copper oleate + *m* cc pyridine gave approximately a solution of *p* percent copper oleate.

	n cc	*m* cc	*p* Percent
(1)	1.9	0.1	4.75
(2)	1.8	0.2	4.50
(3)	1.7	0.3	4.25
(4)	1.6	0.4	4.00
(5)	1.5	0.5	3.75
(6)	1.4	0.6	3.50
(7)	1.3	0.7	3.25
(8)	1.2	0.8	3.00

After standing corked for four hours at room temperature, about 23° C, the lower half of each piece of lead in solutions 1 to 6 was found to be coated with metallic copper, bright and coherent, and the lower half of the liquid in these tubes was no longer blue, but colorless or slightly yellow. After standing a little longer, the entire liquid in these tubes was decolorized and the entire lead surface was coated with copper. In solutions 7 and 8, not the slightest change in the appearance of the solutions or of the lead could be detected after four hours, nor indeed at any subsequent period. After thirty

days, there was still no visible change in the blue copper solutions nor was any copper deposited on the lead. The lead, however, had not so bright a lustre as when put into the liquid and might have been corroded somewhat. A similar experiment was performed, in which the solutions containing the metallic strips were kept in a boiling water-bath. A 1 percent solution of copper oleate in pyridine did not deposit any trace of copper on lead inside of two hours, while 2 percent and 4 percent solutions deposited a bright coherent coating of copper on the lead within two minutes, that is, as soon as they got warm. In a similar way, it was found that within four hours, at 23° C, a bright deposit of coherent metallic copper is formed on metallic cadmium placed in pyridine solutions containing 25 to 2.75 percent of copper oleate, but not at all in 2.5 percent or weaker solutions. At 100° C, a 1.7 percent solution will deposit copper on cadmium, but a 1 percent solution will not. At room temperature, in three hours, metallic zinc completely decolorizes a pyridine solution containing 2.1 percent of copper oleate, the zinc being coated with copper at the same time. A 2.0 percent solution, however, undergoes no change in color even after several weeks' standing, nor is any copper deposited on the zinc.

In view of these facts, which were found out in the latter part of this investigation, the deposition of copper might occur in some of the solvents listed in Table X, if very concentrated solutions of copper oleate were used. To test this in a single case, a solution containing 36 percent of copper oleate in carbon bisulphide was warmed to its boiling-point with lead for several minutes, and allowed to stand in the cold for several hours. The lead was stained black in some places, but no red metallic copper was deposited.

The fact that a 2.1 percent copper oleate solution is decolorized by zinc in three hours, while a 2 percent solution does not react, does not seem to have any parallel among the reactions which occur in aqueous solutions. According to some of the prevalent notions, it would be expected that the more dilute the solution, the quicker it would be decolorized. On

the contrary, the copper, in fact, is held more tightly bound in the weaker solution, so that the lead is not able to replace it at all.

Although the 2.5 percent solution of copper oleate in pyridine does not react with lead at all at room temperature, it can be made to react by adding 0.25 percent more of the copper salt. From this, it appears that the strength with which the solute is held is some inverse function of the quantity in solution. The question at once arose as to whether the addition of any other substance to the 2.5 percent solution of copper oleate would so loosen the hold of the solvent on the copper as to permit the reaction to proceed, as if a larger percentage of copper oleate were present.

To determine this, a 2.5 percent solution of copper oleate in pyridine was prepared and placed in testtubes. To one of them a piece of lead alone was added, but no reaction occurred within two days. To another, some cadmium oleate was added, and in one hour a heavy deposit of bright red copper had formed on the lead. In another portion, some refined glycerine oleate (cotton seed oil) was added with lead, and here too, within an hour, a bright lustrous deposit of copper had formed. In still another portion, some lead oleate was added, with lead, and, as before, the copper deposit appeared within an hour. A considerable amount of lead oleate must be added, as the addition of traces only was found to be ineffective in provoking action. According to the mass law, the addition of lead oleate to the solution should tend to hinder the further solution of metallic lead as oleate in the liquid, but quite the contrary is observed to be the case.

The fact that the presence of lead oleate in the solution accelerates the deposition of copper, as shown in this experiment, explains why a copper oleate solution is decolorized at the bottom first by lead, while the copper deposits more rapidly on the bottom end of the lead strip than at the top. As fast as lead oleate is formed by the reaction on the surface of the metal, it runs down to the bottom of the vessel, and collects there, and on account of its presence, the lower layer

of the liquid more quickly deposits its copper. The decolorization of the liquid proceeds steadily up the tube as far as the top of the lead strip and then stops. This acceleration effect, due to loosening the hold between the solute and solvent, so far surpasses the retardation, by mass action of the lead oleate added, that the latter effect is masked.

Activity of Pure Lead and of Various Alloys

In the experiments recorded above, the lead used was from a lot labeled "test lead, free from silver" from Eimer & Amend. It was melted, cast into bars, and rolled out into thin ribbons, which were cut up, and freshly scraped with a steel tool just before use in each experiment. The attempt to use, instead of this, some ordinary commercial lead, after rolling and scraping, revealed the fact, at once, that the latter material would not precipitate copper from a 5 percent copper oleate solution in pyridine. This inactivity was attributed to the impurity of the lead.

The preparation of specially pure lead by the method of Stas[1] was next undertaken, in order to compare its activity with that of the test lead mentioned above. 365 grams of lead acetate dissolved in 1.5 litres of water, were digested for 100 hours at 40°–50° C, with several strips of pure lead foil. The liquid was filtered and run into a slight excess of a 10 percent solution of pure sulphuric acid. The precipitated lead sulphate was washed by decantation, and digested with an ammoniacal solution of ammonium carbonate in excess. The lead carbonate thus formed was washed thoroughly, drained, dried, and fused with potassium cyanide in a Hessian crucible. The button of lead obtained was remelted, cast into bars, and rolled out for use. This chemically pure lead was found to act upon the 5 percent copper oleate-pyridine solution, but not upon the 2.5 percent solution, precisely as the test lead from Eimer & Amend had done.

A number of experiments were performed to show whether the alloying of various quantities of foreign metals with the

[1] Bull. Acad. roy. Belg., 10, 295.

lead would affect its activity. For this purpose, 1 percent of tin was added to pure lead, and this alloy, boiled with copper oleate in toluene, precipitated metallic copper, but not so rapidly as pure lead. A 2 percent tin alloy with lead acted more slowly with the same solution. With 3 percent of tin, the alloy showed slight traces of copper on its surface, after ten minutes' boiling of the solution. With 5 percent of tin, the metal is slightly blackened after long boiling, but no red copper deposit was obtained.

The addition of 1 percent cadmium to pure lead entirely stopped its action on a dilute solution of copper oleate in toluene. A 5 percent cadmium alloy behaved in the same way.

Alloys of lead with 4.3, 10.5 and 25.1 percent zinc, respectively, precipitate copper easily in bright red lustrous condition.

A 3.7 percent silver alloy with lead was soon coated with copper in the toluene solution. A 10 percent silver alloy precipitates copper more slowly, but the deposit was bright pink in color, and tightly adhering. A 42 percent silver lead alloy was tarnished somewhat.

The addition of 4.2 percent bismuth to pure lead forms an alloy which precipitates copper, lustrous and coherent, from the hot toluene solution of copper oleate. An 8.4 percent bismuth alloy received only a brownish yellow stain.

A 7.4 percent magnesium lead alloy precipitates copper easily and quickly from the hot toluene solution. Alloys containing 10.3 percent and 14.8 percent of magnesium, respectively, do not act on the solution. These latter alloys rapidly decompose hot water, evolving hydrogen gas and disintegrating. On exposure to air for a short time, they crumble to a black brittle powder.

On heating lead and bright metallic copper together for some time in a porcelain crucible, the corners of the copper strip were found to be rounded off, showing that some of the copper had alloyed with the lead. This lead copper alloy

precipitates copper on its surface from the toluene copper oleate solution, but more slowly than pure lead.

Various alloys of lead and antimony containing from 37.4 to 1.2 percent of the latter metal were all found to have no action on the toluene solution of copper oleate.

The presence of 67 percent gold in lead alloy entirely prevents its action on the toluene solution of copper oleate. A 53 percent gold alloy with lead was very slightly tarnished, while a 0.53 percent gold lead alloy slowly took a reddish tinge on heating in the toluene solution of copper oleate, and an 0.18 percent gold lead alloy took a brass color on heating in the same solution.

A 27.7 percent mercury alloy with lead, does not act on a toluene solution of copper oleate, but in a pyridine solution of either copper oleate or copper palmitate it is soon covered with a dull gray pulverulent coating. Pyridine alone has no action on the alloy.

A 20 percent alloy of sodium or potassium with melted lead prepared by melting the metals together under paraffin, received only a slight black tarnish on heating it in the toluene solution of copper oleate. Some alloys of zinc and silver, zinc and magnesium, zinc and copper were tried, but they did not precipitate copper from the toluene solution of copper oleate.

From these experiments, it appears that the alloying of other metals with lead retards or prevents it from reacting with the copper solution, and that the kind of metal and the percentage of it present are important factors. To test this further, a small amount of an alloy of 5 percent tin and 95 percent lead was prepared, cast in a bar, rolled out into a thin ribbon, and cut up into slips 1 by 2 cm for use. 9.68 grams copper oleate and 24.78 grams pyridine were weighed in a flask, forming a 28.1 percent solution of the salt. Portions of this solution were diluted in testtubes with pure pyridine, so as to contain 2, 4, 10, 14, 20, 22, 24, 26 and 28 percent respectively, of the salt, and in each tube was placed a piece of the freshly scraped 5 percent tin alloy. All of the tubes

were corked and set in a beaker of boiling water. As soon as the 26 and 28 percent solutions got hot (within two minutes), the bright red deposit of metallic copper appeared on the metal within. The other solutions were heated for two hours in the boiling water-bath, and although some of the metal slips were slightly tarnished or roughened, no deposit of copper was visible upon them at any time. Here, the very definite strength with which the copper is bound to the solution is clearly shown. The lead similarly is held in its alloy with a definite tenacity. When the concentration of the solution and of the lead in the alloy are adjusted to each other, so that the chemical affinities are in the proper relation, then reaction can occur and not otherwise.

In the experiments already described, it has been shown that the variable factors which aid or prevent chemical action are the temperature, the composition of the solvent, the composition of the metallic salt as to metal and acid radical present, the percentage strength of the salt in the solution, and the percentage composition of the metal or metallic alloy employed for precipitation.

Since the precipitation of copper by lead has been described almost exclusively, another example of this class of reaction was sought in order to see if the case of copper and lead is altogether singular and exceptional.

Precipitation of Mercury by Aluminum from Non-Conducting Solution

Mercury ethyl chloride, HgC_2H_5Cl, dissolves easily in benzol and the conductivity is less than 1.6×10^{-8}, cold or hot. This solution, warmed with metallic aluminum, magnesium, iron, copper, bismuth, antimony and platinum reacts with the aluminum only. Aluminum, alone, reacts easily and a gas is evolved, perhaps butane, the bubbles of which dissolve in the solvent before reaching the surface. The aluminum is rapidly amalgamated, and on removing it from the solution, it is found to have lost its lustre and to be deeply corroded. Dropped into water, the amalgamated metal reacts at once, evolving

hydrogen gas copiously. The precipitation of one metal by another, is therefore, a general reaction, occurring in non-conducting solutions as well as in those which conduct.

Summary

The facts and conclusions of the preceding pages may be summarized as follows:

(1) It was shown by the substitution of benzol for water in aqueous acid solutions, that the activity of acids in inverting sugar, catalyzing esters, and dissolving magnesium can be made to vary entirely independently of the electrolytic conductivity of the solutions.

(2) It has been demonstrated that the replacement of one metal by another metal takes place in molten salts or solutions which are the best of insulators as well as in liquids which are good electrolytes.

(3) In view of these facts and others previously recorded by Kahlenberg[1] it is concluded that the predictions of Arrhenius[2] and Ostwald,[3] to-day widely quoted in text-books,[4] to the effect that electrolytic conduction and chemical activity are proportional, possess no general applicability.

(4) The precipitation of copper from non-conducting liquids and solutions of the copper salts that were studied is accomplished far more readily by means of lead than by sodium, magnesium, iron and other metals commonly considered as more electro-positive than lead. This shows, again, that electrical relations are not always necessarily parallel with chemical affinities.

(5) All other things being equal, the acid radical in the copper salt determines whether the copper will be replaced by lead or not. The oleate, palmitate, and capronate of copper

[1] See references given above.

[2] "Text-book of Electrochemistry," page 182 (1902); Bihang till K. Svensk. Vet.-Ak. Hand. Bd. 8, 13–14 (1884).

[3] Jour. prakt. Chem. 138, 93 (1884).

[4] Nernst: "Theoretical Chemistry," page 519 (1904); Jones: "Theory of Electrolytic Dissociation," pp. 157, 158 (1900); Arnold: "Abriss der allgemeinen oder physikalischen Chemie," p. 103 (1903).

are salts from whose non-conducting solutions, lead precipitates copper easily.

(6) From pure, dry, copper oleate in the molten state, lead deposits copper readily at 100° C.

(7) It was found that from 69 non-conducting solutions of copper oleate, prepared by using as many different solvents, copper is easily precipitated by lead. On the other hand, it was also found that from 14 other non-conducting solutions of copper oleate, lead does not replace copper. This shows that solvents are not "indifferent" even in such cases as those investigated, but are more or less tightly united to the solutes.[1]

(8) It was observed that at a fixed temperature, in a given solvent, a certain definite percentage or more of copper oleate must be present, in order that copper might be precipitated by a given metal. This minimum percentage of copper oleate is different for different solvents, for different metals and for different temperatures. The fact that such a minimum percentage exists in the case of non-conducting solutions has apparently no parallel in the case of aqueous solutions. Again, the precipitation of copper by lead from the copper oleate solutions is greatly facilitated by the presence of oleate of lead, cotton-seed oil or oleate of cadmium, though the presence of mere traces of these substances will not produce such effect.

(9) It was found, in alloying lead with other metals, that widely different percentages of the several metals, are required to stop the action of lead on the copper oleate solution. This shows that the metal added does not act simply as a diluent of the lead, but that the two are really chemically combined, though such alloys are frequently spoken of as solid solutions, a name which commonly suggests the absence of all attraction of a chemical character.

(10) An alloy containing certain proportions of tin and lead reacts at once with a copper oleate solution of a certain definite concentration, and not with a weaker solution. This shows that the copper is held more tightly in the weaker

[1] Compare Kahlenberg: Chem. Zeitung, 29, 81 (1905).

solution than in the stronger, and that the alloy and the solution also are not mere mixtures, but each the product of chemical union between the constituents.

(11) While a number of previous investigators have observed that chemical activity and electrolytic conductivity frequently run parallel to each other, the experiments recorded in this paper, nevertheless, show conclusively that, as a matter of fact, no constant relation exists between electrolytic conductivity and chemical activity; in other words, these do not stand to each other in the relation of cause and effect.

The facts established are readily comprehended when solutions are regarded as chemical unions of solvent and solute.

In conclusion, I wish most cordially to thank Professor Kahlenberg for suggesting to me the work described above, and for the pleasure and profit which the time spent in his laboratory has afforded me.

Laboratory of Physical Chemistry,
University of Wisconsin,
Madison, June, 1906.

THE SOLUBILITY OF CALCIUM SULPHATE IN PHOSPHORIC ACID SOLUTIONS[1]

BY W. C. TABER

The solubility of calcium sulphate in sulphuric acid has been investigated by Struve,[2] and more recently by Cameron and Breazeale.[3] The latter found that there was an increasing solubility of calcium sulphate up to comparatively high concentrations of sulphuric acid, and that at 25° C a maximum was reached with about 75 grams of sulphuric acid per liter. The solubility then decreases in stronger acid solutions.

The solubility of calcium sulphate in nitric and hydrochloric acids has been studied by Banthisch,[4] whose results show that there is an increasing solubility of gypsum in those acids, and it is probable that a maximum point would be reached at higher concentrations of the acids. With 72.36 grams of hydrochloric acid per liter he obtained a solubility of 17.275 grams of gypsum per liter, and with 225.14 grams of nitric acid per liter he obtained a solubility of 20.607 grams of gypsum per liter. Lunge's results[5] with hydrochloric acid at 25° agree well with those of Banthisch, and show a marked tendency to a maximum in the solubility curve.

Banthisch has also studied the solubility effects of monochloracetic acid, and formic acid on calcium sulphate,[6] but the results are too few to make any generalization.

From these investigations of the solubility effects of these different acids on calcium sulphate it is found that there is either a maximum solubility of the salt, or else the curve tends to approach a maximum. Even in the case of sulphuric acid, where it might be expected that the solubility would

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[1] Published by permission of the Secretary of Agriculture.
[2] Zeit. anal. Chem. 9, 34 (1870).
[3] Jour. Phys. Chem. 7, 571 (1903).
[4] Jour. prakt. Chem. 137, 52 (1884).
[5] Jour. Soc. Chem. Ind. 4, 31 (1885).
[6] Jour. prakt. Chem. 137, 52 (1884).

decrease, owing to the presence of a common ion, there is a well defined maximum.

In nearly all cases where the solubility of gypsum has been studied in solutions of electrolytes with no common ion over wide ranges of concentration,[1] the solubility increases with increasing concentration of the electrolyte, until a maximum is reached. At still higher concentrations the solubility decreases again.

In this investigation the solubility of gypsum in various aqueous solutions of phosphoric acid was determined. A series of solutions of phosphoric acid of the strength indicated in the table was saturated with Kahlbaum's calcium sulphate. The bottles containing these solutions were immersed in a constant temperature bath at 25° C and kept in constant agitation for several weeks. The supernatant liquor was analyzed for phosphoric acid, for sulphates, and for calcium. In determining phosphoric acid a few grams of the solution were weighed out, diluted, and an aliquot part taken for analysis, precipitated as ammonium phosphomolybdate, and determined volumetrically. In determining sulphuric acid the sulphate was precipitated by barium chloride in a boiling hot solution. In the precipitation of the calcium from the solution strong in phosphoric acid, alcohol was used, and thus the greater part of the phosphoric acid was held in solution while the lime was precipitated. This precipitated calcium was then dissolved in hydrochloric acid, and precipitated again as oxalate, and weighed as oxide. The sulphate determinations calculated to calcium sulphate showed a tendency to run higher than those derived from the calcium determinations. This may be due to the known tendency of barium sulphate

[1] In NH_4Cl solutions, Cohn: Jour. prakt. Chem. 143, 43 (1887); Cameron and Brown: Jour. Phys. Chem. 9, 210 (1905). In NaCl solutions, Tilden and Shenstone: Proc. Roy. Soc. 38, 331 (1885); Cameron: Jour. Phys. Chem. 5, 556 (1901); Orloff: Jour. Russ. Phys. Chem. Soc. 34, 949 (1902); d'Anselme: Bull. Soc. Chim., Paris, (3) 29, 372 (1903). In $MgCl_2$ solutions, Cameron and Seidell: Jour. Phys. Chem. 5, 643 (1901). In NH_4NO_3 solutions, Cohn: l. c.; Cameron and Brown: l. c. In $NaNO_3$ solutions, Seidell and Smith: Jour. Phys. Chem. 8, 493 (1904).

to carry down foreign material in its precipitation, and to the incomplete precipitation of the calcium by the alcohol. The

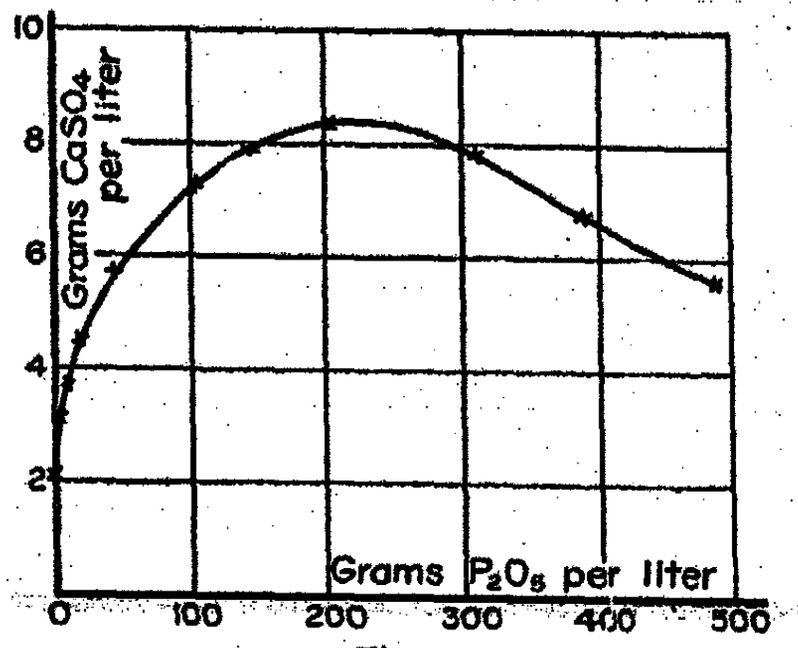


Fig. 1

average variation of these two determinations is about 1 per-cent, if the final solution given in the table be excluded.

The fact that equivalent amounts of lime and sulphuric acid have been found indicates that there is no reaction between phosphoric acid and gypsum to produce a phosphate of calcium, and also a microscopic examination of the solid phase showed only the characteristic crystals of gypsum.

In the following table the calcium sulphate figures are the means of the sulphate and of the calcium determinations.

SOLUBILITY OF GYPSUM IN PHOSPHORIC ACID SOLUTIONS AT 25°

Grams P_2O_5 per liter	Grams $CaSO_4$ per liter	Density of solutions $\frac{25°}{25°}$
0.0	2.126	—
5.0	3.138	1.002
10.5	3.734	1.007
21.4	4.456	1.016
46.3	5.760	1.035
105.3	7.318	1.075
145.1	7.920	1.106
204.9	8.383	1.145
312.0	7.965	1.221
395.7	6.848	1.230
494.6	5.573	1.344

These results show an increasing solubility of gypsum as the concentration of phosphoric acid increases up to about 230 grams of the acid per liter, when there is over 8 grams of gypsum in solution. Like hydrochloric and nitric acids, and unlike sulphuric acid small amounts of phosphoric acid markedly increase the solubility of calcium sulphate in dilute solution. This behavior of sulphuric acid may be attributed to the effect of the common sulphion. As the concentration of the phosphoric acid increases above 230 grams per liter, the curve shows a steady drop, till at about 500 grams of phosphoric acid per liter the solubility of calcium sulphate has decreased to about 5.5 grams per liter.

These results are in accord with the above generalization concerning the effect of electrolytes yielding no ion in common with those from gypsum.

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Washington, D. C.

THE CONSTITUTION OF THE COPPER-TIN ALLOYS

BY E. S. SHEPHERD AND E. BLOUGH

The alloys of copper and tin stand next in importance to those of iron and carbon. Naturally they have been the subject of a great many investigations, some of which have done much toward clearing up the mystery which surrounds the constitution of the series. But, for the most part, the investigations have resulted in increasing the number of data, without in any way permitting of generalizations.

They have been examined as to their density, their heat and electrical conductivities, their electromotive force, and in many other respects, but in nearly every case, the determinations have been made upon bronzes of unknown physical treatment, and as we shall see later, the data obtained apply only to the particular specimens examined. A comparative examination of the data collected shows one thing and no more; namely, that the relation between properties of the different percentage compositions is an additive one. But if one tries to draw any more definite conclusions than that, he is soon lost in a mass of contradictions.

For example, in Fig. 1,[1] if one decides that the measure-

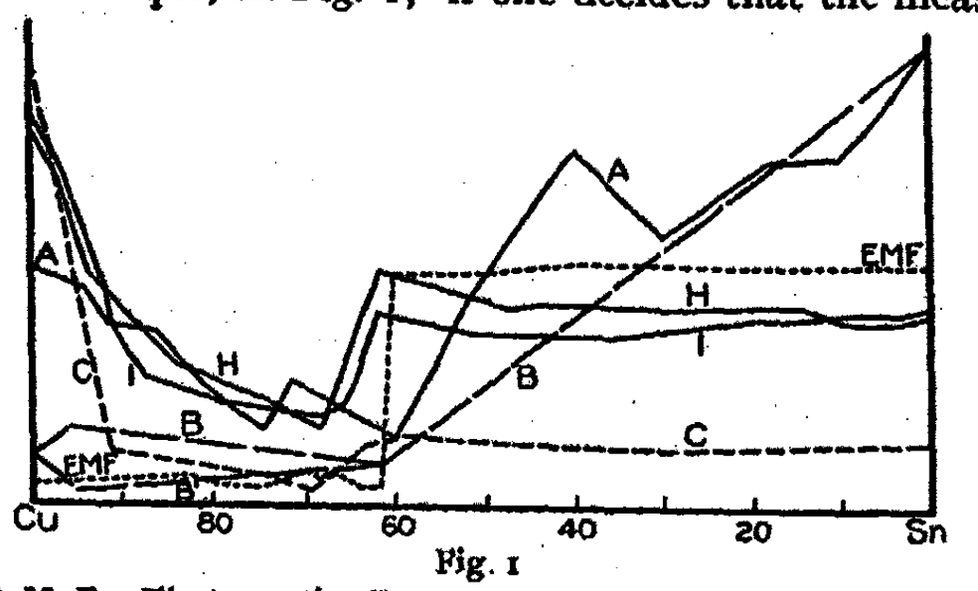


Fig. 1

E. M. F. Electromotive Force
C Electrical Conductivity
B Specific Volume, annealed
I Induction Balance
H Heat Conductivity
A Specific Volume, cast

[1] Quoted with additions from Stansfield. 3d Report of the Alloys Research Com. 1895. For the sake of brevity, we will speak of a bronze as being of a certain percent, meaning thereby the percentage of copper. Thus, a 60 percent bronze contains 60 percent of copper and the rest, 40 percent, tin.

ment of electrical conductivity (C) is to be the criterion of where irregularities occur in the properties of the series, then the singular points will be found at about 61 percent or Cu_3Sn, 68 percent or Cu_4Sn and at 90 percent. However, the heat conductivity (H) shows not only these three points but also an irregularity at 50 percent, as does also the induction balance (I); but the only marked irregularity in the electromotive force (E. M. F.) is at 61 percent, while the maximum tensile strength is at 81 percent.

Density determinations on this series of alloys give quite hopeless results, for while it is not difficult to show that the densities are abnormal, Fig. 1, it is almost impossible to show what they really are. Curve A represents the density of the cast bronzes and curve B that of the annealed bronze. From zero to 61 percent copper, the densities are fairly readily determined, but the large size of the crystals of Cu_3Sn do not readily break down upon annealing, and consequently equilibrium is reached with great slowness.

With bronzes containing more copper than 61 percent, there are two serious obstacles in the way of an accurate determination of the densities. First, the best determinations that we could get showed that the density was practically constant between 61 and 100 percent of copper. Secondly, these alloys dissolve gas while molten, and are never free from blow-holes. It was shown by Riche that the cast and annealed alloys gave different densities, and we were able to show that the density of the quenched alloys was about 0.05 of a unit greater than that of the annealed specimen. In our complete paper we hope to return to this subject, but for the present we can only say that because of the difficulties already mentioned, the densities or specific volumes can in no way help us in determining the constitution.

The first real step in the solution of this problem, was made when Roberts-Austen and Stansfield published their determinations of the cooling curves for the complete series of alloys. It is true that the freezing-point curve had been determined previously by Heycock and Neville and by Le

Chatelier, but neither of them was able to use the results obtained to explain the constitution.

Stansfield's curves, showing the liquidus, and the transformations in the solid, formed the basis upon which Heycock and Neville constructed an approximate equilibrium diagram.

From Stansfield's determination of the liquidus, Fig. 2,[1] we see that it has six branches, from which it follows that there must be six possible solid phases which can crystallize from the molten alloys. An examination of the physical properties as heretofore determined shows that all of the physical properties of this series are abnormal, and the results

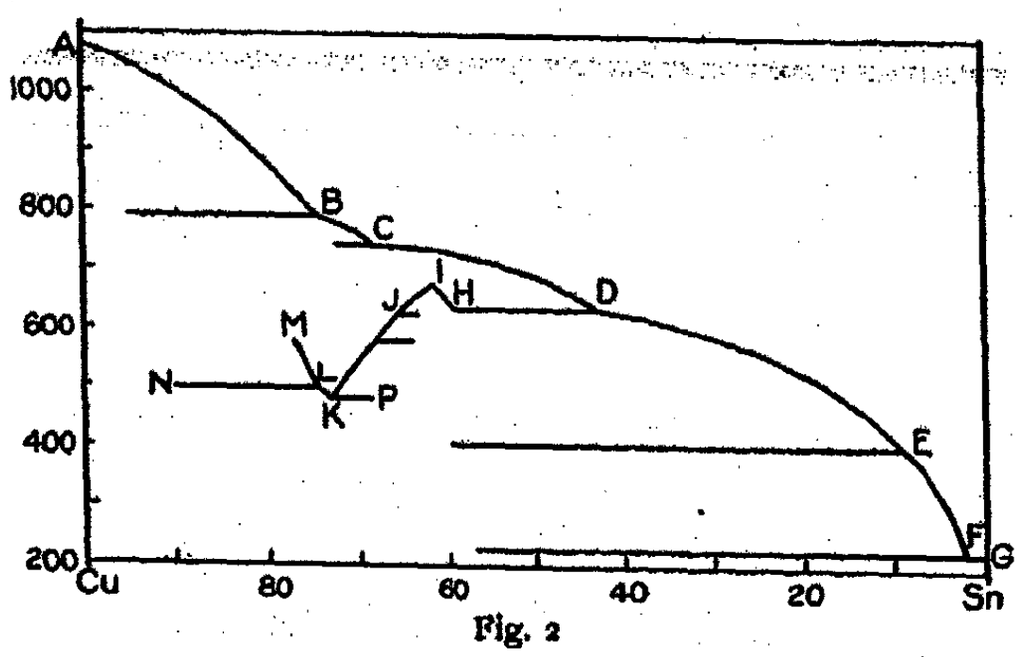


Fig. 2

are fairly conclusive that the abnormality occurs at about 61 percent of copper. But Stansfield's determination of the liquidus shows six branches, and there must be six solid phases possible, so that whereas there are at least six different solid phases, the physical properties show only one of them and it is merely an accident that they show that one. From a comparison of these data we see how useless it is to attack this problem in an unsystematic manner.

Just what may be the composition of these six solid phases cannot be told from the diagram. The method of Tammann will indicate approximately what the compositions may be, but it is open to the objection that it assumes that equilibrium

[1] Fourth Report of the Alloys Research Committee, 1897.

is reached during the time of cooling down of the alloy. As a matter of fact, it frequently takes a considerable length of time for these reactions to take place, and in this case, at least, the method is not a success.

The next method which promises assistance is the analytical method of Bancroft.

We chose lead as the third component, because it was known to form neither compounds nor solid solutions with either copper or tin. In this way it was hoped that the complications might not be increased by adding the third component. Another reason for using lead is that it is easily separated from copper and tin, and allows of very accurate determination. A third component having been decided upon, it was necessary to determine approximately the freezing-point surface for the ternary system. From any mixture from which samples were to be taken for analysis, it was necessary to assure ourselves that the temperature at which the sample was taken was within the field in which the solid phase in question was stable. These points having been determined, analyses were made from the results of which the composition of the solid phases have been calculated.

Certain precautions are necessary in analyzing these alloys, otherwise the results obtained may be quite seriously affected. For lead, tin, and copper the method of solution in nitric acid is used commercially. In fact, however, it is not accurate. Neither lead nor copper can be separated quantitatively from tin by nitric acid. As shown in a previous paper, the stannic oxide always contains lead, and although some writers state that copper can be separated from tin by nitric acid of a certain concentration, reference to the original paper shows that the author worked with bronzes holding never more than 5 percent of tin. On 0.5 gram samples it is not surprising that he was able to detect "only a trace of copper" in his stannic oxide. Previous experience having shown that tin and lead could easily be separated by distilling off the tin as chloride in a stream of HCl gas, it was thought

well to try this method for copper, tin and lead. The results were perfectly satisfactory. The method is as follows:

About 2 grams of the molten alloy are sucked up into a narrow glass tube 2.5 mm in diameter. This sample was then cut into suitable lengths, weighed and placed in a pig similar to the one described in a previous paper. In passing, it should be observed that the glass tubing is always warmed to about the temperature of the alloy before sucking up the sample, and even for samples melting at 900° this soft glass tube, if first heated to redness, can still be used for taking the sample if one works quickly. The alloy is now dissolved by aqua regia varying the proportions of nitric and hydrochloric acids according to the copper content of the alloy. Thus for alloys up to 30 percent copper, one part concentrated HNO_3 to 7–9 of concentrated HCl works more rapidly. Alloys rich in copper will require a greater concentration of nitric acid. Thus for alloys above 60 percent copper, the usual 1 : 4 aqua regia works best. Alloys very rich in lead, 40–90 percent, will require a greater proportion of nitric acid, while those of about 60 percent Pb, 30 percent Sn and 10 percent Cu may require to be first dissolved in diluted nitric acid, brought *nearly* to dryness, and cooled, then concentrated HCl run in and the usual procedure followed.

The alloy being completely dissolved, the pig is placed horizontally in an arsenic furnace, a slow current of air passed through it, and heated gently until completely dry, that is, until the copper chloride turns brown. Of course, if the tin is to be determined, the liquid distilled over must be caught and saved as it will contain a large part of the tin.

The pig having been brought to dryness is now placed in a paraffin bath and heated to 200°, a current of HCl gas being run through the pig to assist in carrying over the tin. At the temperature of boiling sulphur, $CuCl_2$ distils off. In from thirty minutes to an hour, depending on the composition of the alloy, all of the tin will have been carried over. The tip of the outlet tube of the pig and the thistle tube being rinsed into the beaker containing the tin solution, the solution,

which must not be boiled or evaporated, is partially neutralized with ammonia and the tin precipitated with hydrogen sulphide. After washing, it may be ignited to oxide and weighed, or, better, it may be just dissolved in HCl and precipitated as oxide by KNO_3 or $(NH_4)_2SO_4$ as directed in Fresenius. The reason for the second precipitation is to get rid of the excess of chlorides, which are so difficult to wash out of the sulphide and which, if present on ignition, cause a part of the tin to volatilize. The determination of the tin is by no means as accurate as that of the other two metals.

The residue of copper and lead chlorides in the pig is now washed, put into an evaporating dish, and the pig rinsed with conc. HCl to remove the adherent lead chloride. After the excess of HCl has been evaporated, strong HNO_3 is added and the chlorides evaporated to dryness, more conc. HNO_3 added and again evaporated until the lead and copper chlorides are completely changed to nitrates. With small quantities of lead one or at most two evaporations will suffice. For larger amounts of lead a third evaporation will be necessary.

The nitrates of lead and copper are now taken up with water containing about 10 cc of conc. HNO_3, and electrolyzed either in a Classen dish, which is tedious, or with a rotating cathode.

When no more lead or copper is precipitated, the solution is evaporated to dryness, about 1 gram $NaNO_3$ added, taken up with 25 cc of water and again electrolyzed. By this process, all of the lead and copper are precipitated and the only error in the determination of these two components is the error of weighing. With the tin, on the other hand, an error of 0.2–0.4 percent results even with careful work, and it is for that reason that we felt justified, after making some preliminary experiments, in getting tin by difference and basing our calculations on the figures for lead and copper. That this is quite justified will appear in the course of the analyses.

It should be stated that, if instead of adding 10 cc of KNO_3 to the nitrates, as above, 0.5 cc HNO_3 and about 10 grams $NaNO_3$ are added, the first electrolysis will run out

practically all of the lead and copper (start slowly), and for ordinary work the concentration and second electrolysis can be omitted. There seldom remains over 0.05 percent of either metal in the electrolyte, under these circumstances.

The alloys were melted in an atmosphere of coal gas, so that except for a deposit of carbon at high temperatures, the surface of the alloy remained bright throughout the course of the experiment.

The furnace used was a specially constructed Fletcher gas furnace made for us by the Buffalo Dental Manufacturing Company, and of such dimensions that a 00 graphite crucible just fitted tightly against the opening in the lid, leaving the whole mouth of the crucible free for manipulation.

Results.—The following results were obtained for the branch AB of the liquidus.

	Concentrations		Percent Sn in solid phase
	Initial	Final	
1	Cu, 89.89 Pb, 5.02 Sn, 5.09	Cu, 83.04 Pb, 8.37 Sn, 8.59	—0.16
2	Cu, 78.75 Pb, 10.54 Sn, 10.71	Cu, 72.14 Pb, 14.58 Sn, 13.28	+4.00
3	Cu, 79.98 Pb, 10.09 Sn, 9.93	Cu, 73.39 Pb, 14.02 Sn, 12.59	+2.42
	Cu, 75.93 Pb, 11.46 Sn, 12.61	Cu, 70.28 Pb, 14.20 Sn, 15.52	+0.442

The minus sign indicates that 0.16 percent lead crystallized with the copper. This is doubtless due to analytical error. Thus by analytical methods we have proved positively that copper forms a solid solution with tin and we have also shown that the percentage of tin so absorbed varies over at least 5 percent. It will be shown in the metallographic section

that, on careful annealing, copper will absorb as much as 13 percent of tin, and the variation found on analysis is probably due to the different rates of crystallization. It was not possible to wait for equilibrium to be reached.

The limiting concentration of tin in copper could be shown analytically also, if necessary, by allowing a certain amount of crystals to form and then holding the temperature constant until equilibrium had been reached. Of course, where a compound crystallizes, this difficulty is not encountered. Nor is it so serious when working at lower temperatures. The α-crystals of Heycock and Neville are therefore as they had suspected, a solid solution of tin and copper, the limiting concentration on rapid cooling being about 5 percent of tin.

The following results were obtained for branch BC, of the liquidus:

	Concentrations		Percent Cu in solid phase
	Initial	Final	
1	Cu, 69.14 Pb, 1.64 Sn, 29.22	Cu, 67.34 Pb, 2.00 Sn, 30.66	77.31
2	Cu, 70.33 Pb, 2.09 Sn, 27.58	Cu, 68.49 Pb, 2.89 Sn, 28.62	75.10
3	Cu, 68.86 Pb, 7.46 Sn, 23.68	Cu, 55.99 Pb, 23.63 Sn, 20.38	74.80
4	Cu, 67.31 Pb, 4.87 Sn, 7.82	Cu, 64.37 Pb, 7.40 Sn, 28.23	73.09
5	Cu, 66.55 Pb, 3.09 Sn, 30.36	Cu, 65.68 Pb, 3.69 Sn, 30.63	70.73

From the above results we see that the crystals which separate from bronzes containing between 68 and 74 percent

of copper, are a solid solution in which the copper content varies between 70 and 78 percent. As is to be expected the alloys richer in copper yielded β-crystals richer in copper.

For the branch CD of the liquidus, the following results were obtained:

	Concentrations		Percent Cu in solid phase
	Initial	Final	
1	Cu, 59.50 Pb, 3.37 Sn, 37.13	Cu, 58.11 Pb, 3.98 Sn, 37.91	67.76
2	Cu, 62.11 Pb, 2.86 Sn, 35.03	Cu, 61.10 Pb, 3.46 Sn, 35.44	66.93
3	Cu, 59.45 Pb, 3.63 Sn, 36.92	Cu, 57.15 Pb, 4.87 Sn, 37.98	66.41
4	Cu, 54.99 Pb, 4.98 Sn, 40.03	Cu, 52.28 Pb, 6.34 Sn, 41.38	64.90
5	Cu, 62.02 Pb, 1.06 Sn, 36.92	Cu, 61.12 Pb, 1.47 Sn, 37.41	64.39
6	Cu, 62.73 Pb, 1.08 Sn, 36.19	Cu, 61.39 Pb, 1.97 Sn, 36.64	64.35
7	Cu, 59.98 Pb, 4.11 Sn, 35.91	Cu, 56.92 Pb, 7.35 Sn, 35.73	63.85
8	Cu, 54.59 Pb, 4.67 Sn, 40.74	Cu, 49.75 Pb, 8.31 Sn, 41.94	60.80

The results here show that the γ-crystals are a solid solution of tin in copper, the percent of copper varying between 60 and 68 percent. Many analyses were made necessary by the fact that the crystals being small the mother-liquor which one can pipette off, becomes very scanty before any great

change of concentration has occurred. And it was also desirable to settle beyond question that the γ-crystals were mixed crystals and not a compound.

Branch DE of the liquidus:

	Concentrations		Percent Cu in solid phase
	Initial[1]	Final	
1	Cu, 30.0 Pb, 12.0 Sn, 58.0	Cu, 14.23 Pb, 17.82 Sn, 67.95	62.50
2	Cu, 34.0 Pb, 10.0 Sn, 56.0	Cu, 14.64 Pb, 17.24 Sn, 68.12	60.91
3	Cu, 30.0 Pb, 15.0 Sn, 55.0	Cu, 15.64 Pb, 22.08 Sn, 62.28	60.43

Mean, 61.3
Theory for Cu_3Sn, 61.6

When it is remembered that these were the first analyses made and that the extrapolation is across a range of 25 to 30 percent, we feel justified in concluding that the solid phase which separates from bronzes containing between 8 and 43 percent copper is the compound Cu_3Sn.

In the ternary system the change from the field of the phase CD to that of the field for DE is readily noticeable with the naked eye. With a little practice the location of the boundary curve between the two can be easily detected to within 3 percent on ingots which have not cooled too rapidly. The presence of the lead makes the large plates of Cu_3Sn stand out very sharply on the surface of the ingots.

An examination of the ternary diagram shows that the phase crystallizing along branch EF of the liquidus, Fig. 2, exists in a comparatively small field. It would be very

[1] This series of initial concentrations were weighed out to milligrams on hundred gram lots, so that no analysis was deemed necessary. This assumption was confirmed by analysis.

difficult to determine this phase by starting with the initial concentration lying within the field for the crystallization of the phase in question. The range of concentration possible is not over 3 percent and the location of the field is such that a slight error in analysis would result in an enormous error in the calculation so that it is necessary to use some other method. From the most advantageous point which could be chosen an error of 0.2 percent in the analysis would extrapolate to an error of between 5 and 20 percent in the calculation of the position of the solid phase. The method which must be used is a combination of the analytical method with a method of transformation. It is found possible to start with the initial concentration lying outside of the field for the solid phase and if properly selected it is possible to cause the first phase which separates to disappear and the position of the melt to enter the field of the phase whose position is sought. This method is so helpful where one has to deal with small fields, that a word about it may not be out of place.

Let us suppose that we wish to determine analytically the composition of the phase which is stable in field IV of Fig 3. We know that the phase is of a composition approaching

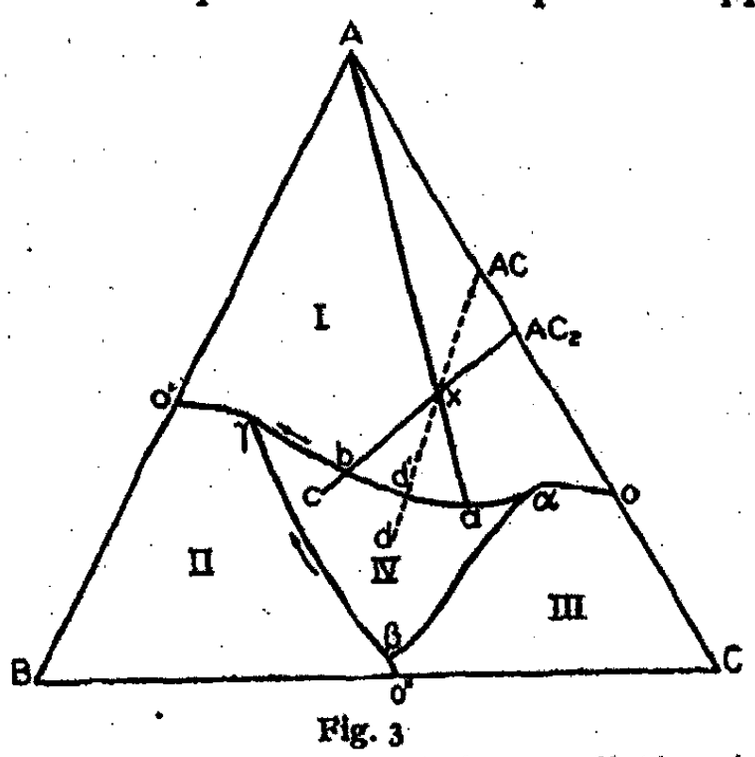


Fig. 3

that of the point AC_2, the problem being to distinguish whether it is the phase AC_2 or the neighboring compositions AC and

AC_3. If we know the freezing-point surface of the field, α, β, γ, we can select a temperature and composition such that by holding the temperature constant at some point within field IV all of the first crystals which separated from the melt, will be transformed into crystals which are stable within field IV. Thus on cooling an alloy of the composition x, crystals of A will first separate along xa. When the mother-liquor reaches the composition a, AC_2 begins to separate. As the temperature falls, the composition of the melt moves along the boundary curve towards the lower quintuple point γ. This change can occur only by A redissolving as AC_2 separates. This reaction progresses until at the composition indicated by b, all A has disappeared and we have left only the solid phase AC_2 and the melt. Further cooling will tend to move the composition of the melt along the line xbc.[1] The path followed by the changing composition of the mother-liquor is indicated by the heavy lines $xabc$.

If therefore we hold the alloy x for a sufficiently long time at the temperature c, and if the alloy has been properly stirred to break up the larger masses and insure equilibrium, an analysis of the mother-liquor and the solid (which may be mixed with mother-liquor) will show the composition of the solid phase. If our surmise as to the composition of the solid phase has been correct, then the extrapolation will indicate AC_2. If the phase is AC, the composition of the melt will have reached the point d instead of progressing to c. Thus by choosing several compositions and analyzing, we can arrive at the composition of the solid phase. If the compound were ternary, the problem would be attacked in a similar way.

It may be objected that the method necessitates some foreknowledge of the composition of the phase in question, but this objection is not as reasonable as it might seem. We are dealing with a case in which it is impossible to separate and analyze the crystals. The microscopic methods will help, but would be very delicate for such a case. Since there is not

[1] Geer: Jour. Phys. Chem. 8, 257 (1904).

sufficient change of concentration inside the field to allow of accurate extrapolation, the transformation method suggested is the only one now available.

It was mentioned above, that the analysis of the solid, with whatever mother-liquid it might hold, would be desirable. This gives us three points for determining the composition of the phase. First, the initial concentration; second, the mother-liquid, plus a small amount of admixed solid; and third, the solid, with a greater or less amount of mother-liquid. This last composition can be made to approach much nearer to the composition of the solid phase than does the initial concentration, thus increasing the accuracy without an increase in the experimental difficulties.

The limitations to the application of this method of transformation are those of manipulation. If an alloy is too rich in copper, as Cu 30 percent, Pb 1 percent, Sn 69 percent, there will not be enough mother-liquor left at 227° to pipette off, nor will the change from Cu_3Sn to the next tin-rich phase be rapid enough for practical purposes. Even a 20 percent copper alloy had not completely changed over, on holding for five days at 227°, although the mass of Cu_3Sn crystals was removed, broken up in a mortar and stirred into the melt. By very careful work we were able to obtain the following results:

It will be seen that some of the results show percentages of copper which are out of the region for the phase studied. This means that crystals of the solid phase were sucked up with the mother-liquor. This is not an uncommon occurrence where the crystals are small. Thus, in certain analyses, the sample pipetted off showed an increase in copper and a decrease in lead, *i. e.*, a reversal, while a third sample taken at a somewhat lower temperature fell back into line and all three points lay on the same straight line. It is evident that if more crystals than mother-liquid are sucked up in the sample, the concentration may vary anywhere between that of the pure solid phase and the initial concentration.

Of all of these analyses, the last three were by far the

	Concentrations		Percent Cu in solid phase
	Initial	Final	
1	Cu, 13.907 Pb, 4.046 Sn, 82.047	Cu, 12.513 Pb, 4.287 Sn, 83.200	37.25
2	Cu, 14.248 Pb, 4.645 Sn, 81.107	Cu, 2.734 Pb, 7.237 Sn, 89.929	34.82
3	Cu, 18.46 Pb, 2.23 Sn, 79.31	Cu, 5.81 Pb, 3.43 Sn, 90.66	41.7
4	Cu, 18.10 Pb, 3.69 Sn, 78.21	Cu, 11.19 Pb, 4.75 Sn, 84.06	42.2
5	Cu, 12.88 Pb, 3.07 Sn, 84.05	Cu, 6.06 Pb, 3.81 Sn, 90.19	41.1
6	Cu, 21.231 Pb, 4.154 Sn, 74.615	Cu, 2.875 Pb, 8.777 Sn, 88.348	37.72
7	Cu, 21.301 Pb, 3.091 Sn, 75.608	Cu, 4.048 Pb, 6.149 Sn, 89.803	38.74
8	Cu, 24.219 Pb, 2.513 Sn, 73.268	Cu, 2.177 Pb, 5.846 Sn, 91.977	38.53

best. The conditions were better than in the first five, and the changes of concentration were greater. All of them agree in showing that the solid phase is certainly not CuSn, and that its composition does not fall at any simple molecular proportion.

Since the temperature limits of the field for this phase are quite small, it was thought necessary to use some kind of a thermostat, which would be more constant than the electric furnace. Consequently a large boiling tube was lowered into the furnace. This tube had suspended in it a crucible containing the alloy. A simple condenser at the top served to

return the condensed liquid. Boiling quinoline gives a very constant temperature of about 230°, which temperature was the most advantageous for the investigation of this phase. The boiling liquid serves to balance the variations in voltage on the line, and the electrical heating minimizes the danger from fire, should the boiling tube break. Metal tubes were not found to be satisfactory. With this arrangement, it was found possible to keep the alloys at the temperature of boiling quinoline for weeks at a time. As a result of all of the analyses, we are able to say definitely that of all the phases which can separate from their respective branches of the liquidus, only one is a definite compound. The remainder are solid solutions whose compositions vary with the temperature.

III. Microscopic study

In what has gone before, we have considered only such phases as might exist in contact with the melt. It will now be worth while to investigate the significance of the evolutions of heat detected in the solid alloys.

If we examine the heat changes shown in Stansfield's diagram, Fig. 2, the curve HIJKLM suggests at once changes in the solid which resemble those which occur in the freezing of a liquid alloy. It must be remembered that this diagram was obtained under certain fixed conditions, and that certain assumptions were made, which may or may not have been warranted.

In the first place, all of these data were obtained by means of cooling curves. This means that the reactions were liable to supercooling. Very careful measurements made with the aid of heating curves have shown that supercooling does occur in the determination of these temperatures. Thus on the heating curves the inversion temperatures did not vary more than two-tenths of a degree (measuring directly to microvolts) while the cooling curves showed often as much as 20° supercooling. It follows therefore, that the points actually determined by Stansfield and by Heycock and Neville, will have to be revised.

During our study of these temperatures, we were able to establish that branches NL and KP of the curve given in Fig. 3 were continuous and that the branch LM is not properly located.

A second assumption made in the determination of the constitution of these alloys is that the heat changes observed are necessarily the *only* changes which here exist. There is *no warrant* for such an assumption.

Before examining the results of our investigations, we must give attention to the equilibrium diagram worked out by Heycock and Neville. This diagram is reproduced in Fig. 4.

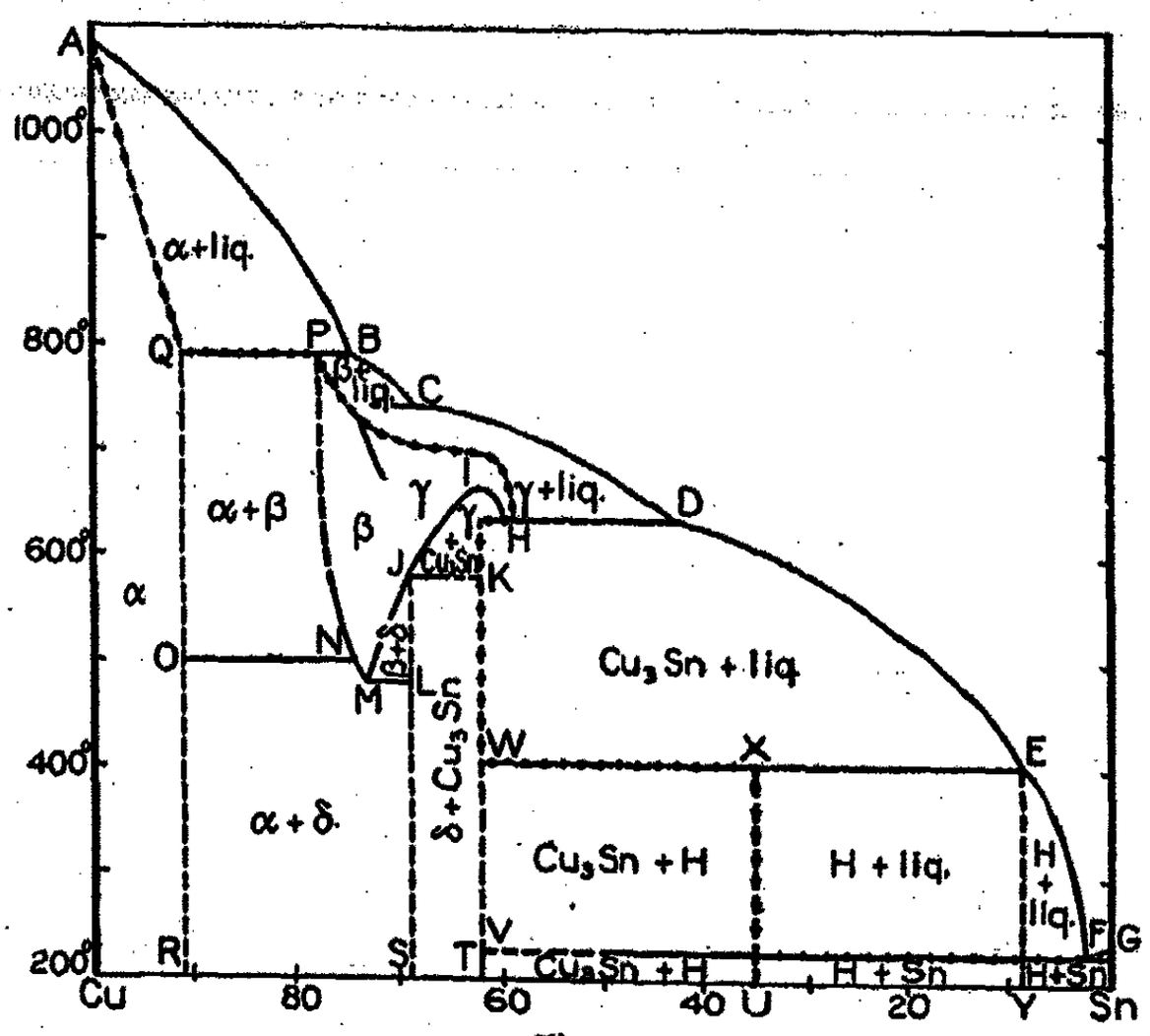


Fig. 4

Assuming the temperatures indicated by Stansfield to be correct, and that the inversions there indicated were the *only* ones, these two pioneers worked out what seemed to them to be the correct interpretation of the data.

They readily saw that copper crystallized from the copper-rich bronzes as a solid solution, and they placed the

limiting concentration at 9 percent of tin. They did not determine whether or not this limit was changed by change of temperature after the alloy had become solid. Consequently, they drew the line QR vertical.

The shape of the triangular field PHIJMN was so suggestive that they were a little misled as to the nature of the alloys in this region. The V shape of this field suggested that the alloys were a homogeneous solid solution which was in contact with the γ-crystals on one side, and with the α-crystals on the other. That being true, the point M becomes the eutectoid concentration and temperature. Of course it is absolutely necessary that the temperatures of line LM and NO be identical, otherwise we would have α, β, δ, and vapor existing over the range of temperatures of MN, a condition which is impossible from a theoretical point of view.

These investigators were unable to locate within the field PHIJMN the region for pure β, pure γ, and the mixtures of β and γ. It will be found, by trying to draw in the imaginary limits of these fields, that there is no arrangement which will satisfy the demands of the theory. It becomes evident therefore, that either their microscopic data, or the pyrometric data, or both must be in error.

When we look for the reason for these very skilful investigators having been unable to solve this problem, we find it in the second of the assumptions mentioned above. In investigating this region, they assumed that the only changes were those indicated by the pyrometer. Consequently, by preparing specimens by quenching from temperatures in this region, they chose only those temperatures which were indicated by the heat changes. This error is not entirely the fault of these particular men but is one which they learned from their predecessors in this kind of work. In fact, there has not been any investigation of the much studied iron-carbon alloys in which this same blunder has not occurred. It was only natural for Heycock and Neville to make a similar mistake.

In undertaking the study of these alloys it seemed to us that the only way to be sure that nothing was overlooked was to make the study thorough. It was decided that it would be better to examine every percentage, at intervals of 10°, throughout this region. In order to do this, it was necessary to arrange a thermostat in which a high temperature could be maintained constant for long periods of time. This result was finally obtained by means of an electrically heated lead bath, which was equipped with a stirrer. The pyrometer placed in the lead gave the temperature, and the ingots treated were protected by means of shields of Jena glass. A current of coal gas prevented oxidation. The ingots after having been held at the desired temperature for a sufficiently long time were removed and quenched instantly by immersing in a large vessel of cold water. The ingots being relatively small, and the time which elapsed between their removal from the bath and the time they reached the water being much less than a second, we were able to fix the structure present in the alloy at the temperature in question. Duplicates assured us that the method was reliable. As a result of our investigations the diagram submitted in Fig. 5 is thought to express the constitution of the copper-tin alloys. In Fig. 6 the crosses indicate the compositions and temperatures at which annealings and quenchings were made.

In Fig. 2 it is seen that the pyrometer shows the presence of the quadruple point as far over as 95 percent of copper. However, this is a case of quite rapid cooling. In Fig. 5 we have shown this quadruple point only as far as 90 percent. The reason for doing so is that investigations of the curve at lower temperatures would seem to require that for conditions of equilibrium the quadruple point can scarcely extend beyond 90 percent of copper. This likewise, when annealed for a considerable time at temperatures between 200° and 700°, becomes perfectly homogeneous as far over as 87 percent of copper.

Field I is the region for the pure α-crystals of which the

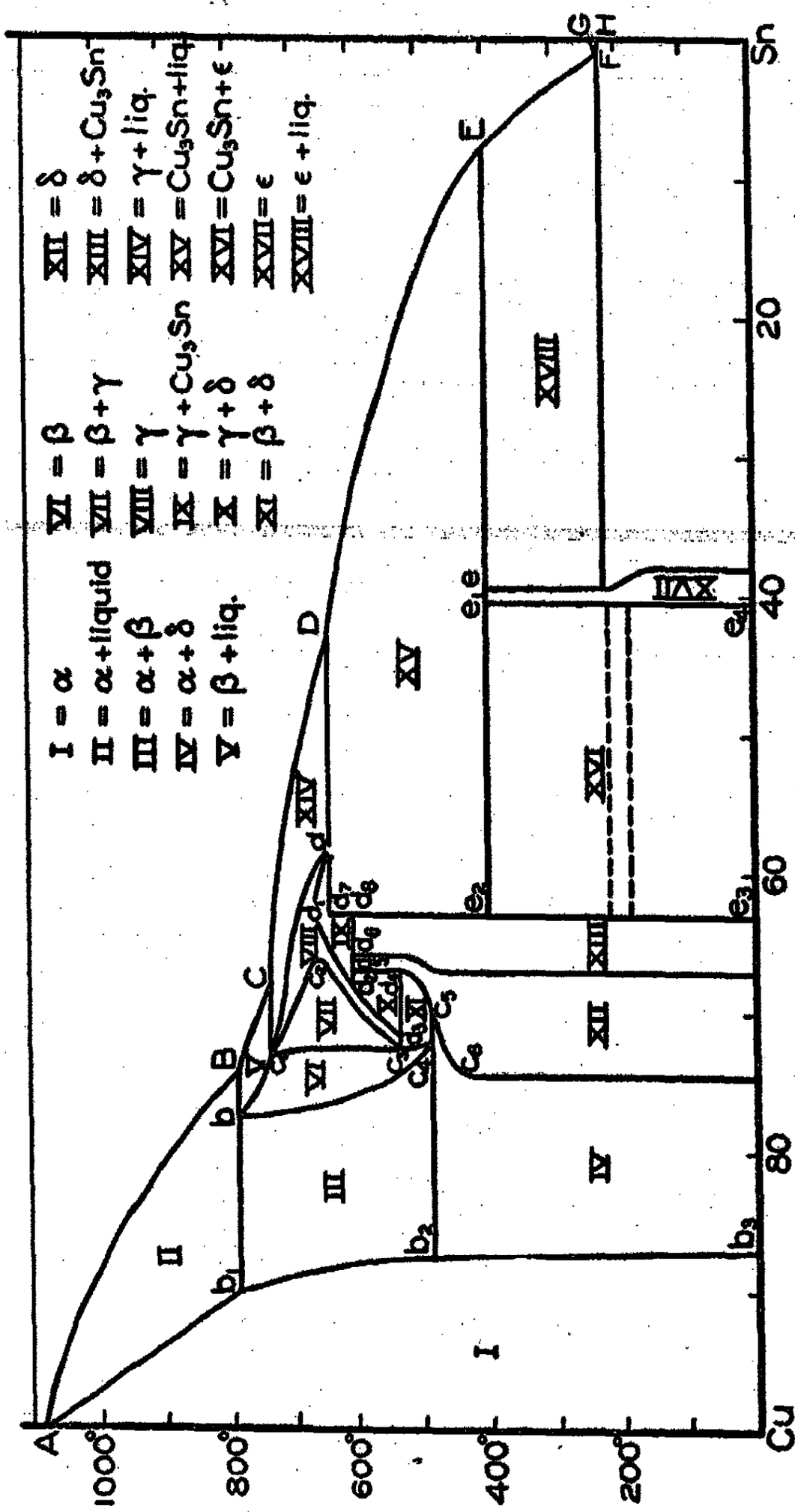

Sn
Cu
A
G
H
F
E
D
C
B
I = α
II = α+liquid
III = α+β
IV = α+δ
V = β+liq.
VI = β
VII = β+γ
VIII = γ
IX = γ+Cu3Sn
X = γ+δ
XI = β+δ
XII = δ
XIII = δ+Cu3Sn
XIV = γ+liq.
XV = Cu3Sn+liq.
XVI = Cu3Sn+ε
XVII = ε
XVIII = ε+liq.
1000°
800°
600°
400°
200°
20
40
60
80

Fig. 5

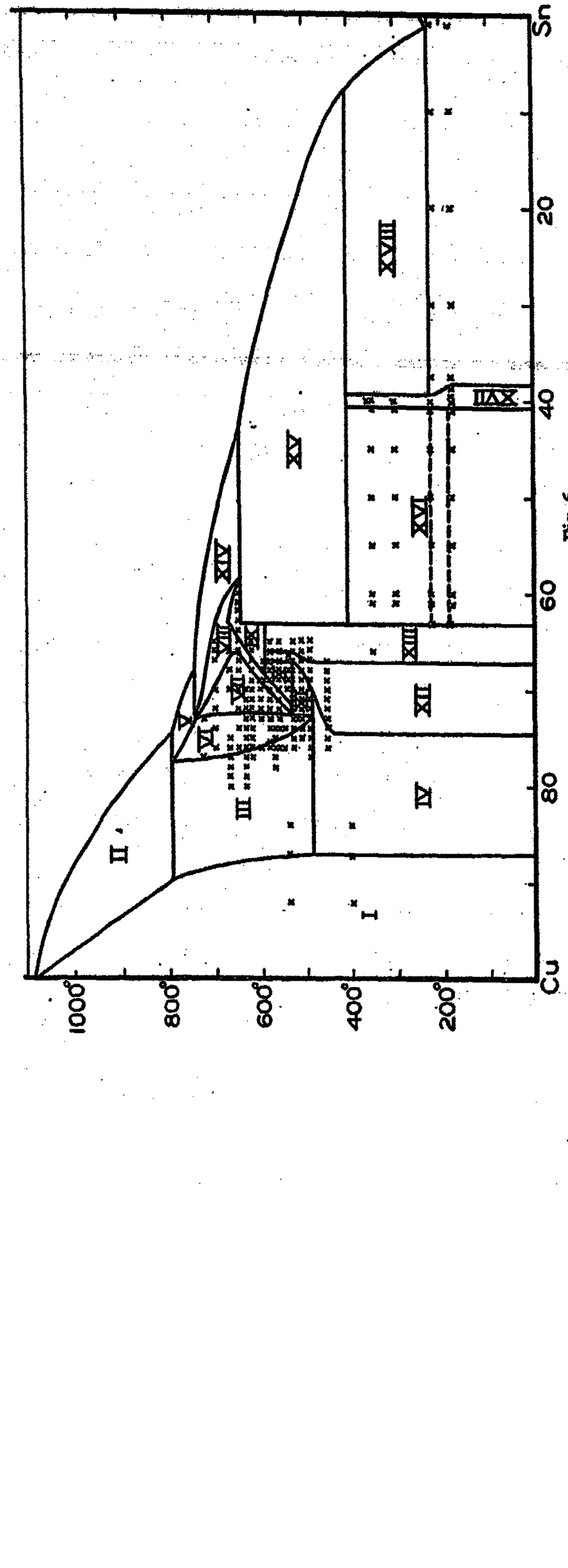

Sn
20
40
60
80
Cu
1000°
800°
600°
400°
200°
I
II
III
IV
V
VI
VII
VIII
IX
X
XI
XII
XIII
XIV
XV
XVI
XVII
XVIII

Fig. 6

tin concentration is seen to vary with temperature and to reach the maximum of about 13 percent.

Field II is the field in which α-crystals are stable in contact with the melt. As indicated by the line Bb_1, alloys with these concentrations consist of two phases, α and β.

As indicated by the line c_5b_2 the β-crystals break down at a temperature of 486° with the formation of the succeeding phase which we have called δ.

Field V is the region for β-crystals in contact with the melt.

Field VI gives the region for homogeneous β.

Field VII is the region for a mixture of the crystals β and γ.

Field VIII is the region for pure γ. This field is very peculiar in shape, but the existence of the slender arm $c_2c_3d_1$ has been verified very carefully. The chief trouble in determining the relation in this region lies in the fact that it is so very narrow. On this account it is likely to be missed unless specimens are taken at least for every percent of change in concentration. Once the field is located it cannot be mistaken for the region on either side of it. The branch $c_2c_3d_3d_1$ is of course homogeneous. But Field VII consists very clearly of a mixture of yellow and white crystals, β and γ. However, region X differs from region VII, and consists wholly of white crystals whose behavior shows the alloys to be a mixture of two kinds of crystals. The differences are distinctly marked and warrant interpreting this region as consisting of two solid phases.

Below the line d_3d_4 the change of the structure in the alloy is very striking. Instead of consisting of the mixture of the white crystals in Field X, we have now a mixture of brilliant yellow crystals in the white matrix. This change is so striking and so impossible of explanation, according to the diagram of Heycock and Neville, that we were led to believe in the existence of the line d_3d_4 long before we were able to verify it experimentally.

The phase δ, which is formed entirely through transformation in the solid, was for a long time considered to be the compound Cu_4Sn. That such is not the case is shown by the fact that the composition Cu_4Sn is not homogeneous over the temperatures at which it is necessary for the compound to exist. It is found that alloys having 1 percent less copper than the composition Cu_4Sn are homogeneous, and we have, therefore, designated the phase merely as δ. It is a solid solution whose composition varies remarkably with changing temperatures as indicated by the lines bounding Field XII. Thus while alloys containing between 70 to 74 percent of copper are inhomogeneous at temperatures above $d_4c_5c_6$, they are perfectly homogeneous below the lines of c_5c_6. We were able to say that the lines c_6c_7, d_6, and d_7 fall almost vertically, the variation being not greater than 1 percent in composition.

Field XIII consists of a mixture of δ and Cu_3Sn resulting from the breaking down of the γ-crystals along the line d_2d_8.

Our results agree with those of Heycock and Neville as to the breaking down of γ with the formation of Cu_3Sn at the composition of that compound.

Field XV is the region for Cu_3Sn already in contact with the melt.

Field XVI is the region for Cu_3Sn and the next phase ε.

As we found from analytical data, this phase ε could not be the compound CuSn, and a careful study of the annealed and quenched alloy has shown it to occupy the region of Field XVII.

Field XVIII is the region for ε in contact with the melt.

Whether or not pure tin or a solid solution separates along the liquidus FG is a matter of little importance.

In addition to the changes in the solid which have been recorded for the copper-rich alloys, we found two other heat changes in the alloys containing from 41 to 61.5 percent of copper. The first of these changes is at 218° and occurs at the same temperature in all of the above-mentioned concentrations. The second change is likewise one at constant temperature and is found at 182°.

The heat effect is small in the lower change but quite large in that at 218°. At present we are unable to give a satisfactory explanation as to the cause of these changes. At first sight one might attribute the upper change to lag in the eutectic change, but the 218° point is very distinct from that of the eutectic. On the other hand, the suggestion that the 182° change is related to the supposed allotropic modification of tin, at 170°, is not borne out by the fact that these two changes do not occur in the alloys in which tin is *one* of the solid phases. Even when the 25 percent alloy is poured into water, and the resulting shot (which are of a very fine-grained structure) are annealed for three weeks at 150°, there is no evidence of these two heat changes on the heating or cooling curves. Nor are these two changes to be detected in the alloys richer in copper than Cu_8Sn, *i. e.*, 61.5 percent.

Our attention was first directed to these phenomena by the change in microstructure which the alloys undergo when annealed for a long time at about 180°. For the present, however, it seems better to publish the data available, and leave the discussion of these relatively unimportant changes for the completed paper.

In our complete paper we will publish the photographs showing the structures which are characteristic of each region, and show more in detail the method of investigation. For the present, the diagram submitted will suffice to indicate the nature of these important alloys as well as the value of more *systematic* investigation of alloys. The great importance of the time factor in establishing equilibrium relations is emphasized by the difference between this diagram and those previously published. The assumption made by the earlier investigators, *i. e.*, that the reactions involved were instantaneous, has been disproved. It has also been shown that the pyrometric evidence alone is not sufficient to establish such diagrams. These assumptions are so obviously in error that there would seem to be no need of calling attention to them, but the literature shows them to have been made by nearly every student of alloys.

The general results of this paper are as follows:

1. The phases which can coexist with the melt are the α, β, and γ solid solutions, the compound Cu_3Sn, the ϵ solid solution, and pure tin.

2. Below 600° the δ solid solution can exist. This phase was previously supposed to be the compound Cu_4Sn.

3. The complete concentration-temperature diagram has been worked out for temperatures above 219°.

4. Mixtures of Cu_3Sn and the ϵ crystals show heat effects at 218° and at 182°. The nature of these changes is still in doubt.

In conclusion, we wish to thank Professor Bancroft, who has directed and encouraged this investigation since it was begun some three years ago. His kindly criticism has always been available, and without it, it is very doubtful whether or not the results obtained would have been possible.

The expenses of the investigation have been met by grants from the Carnegie Institution of Washington, to which full credit must be given. A part of the pyrometric work was done in the Geophysical Laboratory of the Carnegie Institution, and we wish to thank Dr A. L. Day for the facilities afforded.

Cornell University.

IDENTIFICATION OF SOLID PHASES

BY L. F. HAWLEY

I. Lead hydroxide and lead carbonate

Salvadori[1] has shown that a salt of the composition, $PbO_2H_2.2PbCO_3$, is formed when lead carbonate is boiled with water or when lead sulphate or chloride is boiled with aqueous sodium carbonate. These experiments seem to point to white lead being a definite compound having the formula $PbO_2H_2.2PbCO_3$. It is possible however that there might be a series of solid solutions of which the apparent compound was merely the last term. This possibility was the more to be considered because the obtaining of a definite composition does not seem to be altogether easy when white lead is made electrolytically.[2] It seemed desirable therefore to check the composition of white lead by another method, the solubility method.[3] Neither lead carbonate nor lead hydroxide is soluble enough in water to make the usual form of the method applicable, but the solubility in sodium acetate solutions is sufficient. If the ratio of water to sodium acetate be kept constant, the sodium acetate solution may be considered as a new solvent and we can treat the system as a three-component one.

Lead carbonate and lead oxide were taken as the constituents to be added to the sodium acetate solution. Pure lead hydroxide is difficult to prepare and the oxide was used instead after it had been found that lead oxide hydrates readily when in contact with lead carbonate. Mixtures of lead oxide and carbonate in varying proportions were left in contact with 20 percent sodium acetate solutions at 75° for from twelve to fourteen hours. The solutions were then allowed to stand at ordinary temperature for several hours, after which 50 cc portions were pipetted off and the lead in solution determined as sulphate. The undissolved solids were washed in water

[1] Gazz. chim. Ital., 24, I, 87 (1904).

[2] Isenburg: Zeit. Elektrochemie, 9, 275 (1903).

[3] Miller and Kenrick: Jour. Phys. Chem., 7, 259 (1903).

free from carbon dioxide, dried in a desiccator over potassium hydroxide and analyzed for lead oxide, water and carbon dioxide.

The results obtained are shown in Fig. 1, the ordinates being the amount of lead in solution and the abscissas the molecular percentages of PbO and $PbCO_3$ in the solid phase or phases.

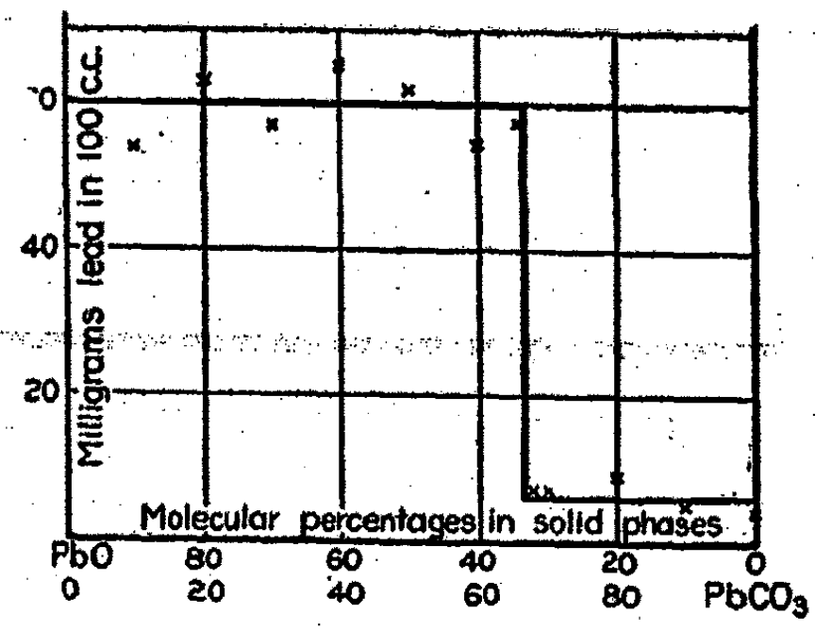


Fig. 1

This diagram shows that there are no solid solutions and that white lead is a definite compound containing two of lead carbonate to one of lead oxide. The water determination shows that the formula is $PbO_2H_2.2PbCO_3$. An interesting check on this was obtained in the case of mixtures rich in lead oxide. The amount of oxide changed to hydroxide is exactly equivalent to one-half the lead carbonate present. When mixtures of lead oxide and lead carbonate are treated with water at ordinary temperatures, the possible solid phases are PbO, $PbO_2H_2.2PbCO_3$, $PbCO_3$.

II. Thallium sulphide and stannic sulphide

When thallium sulphide and stannic sulphide are precipitated together, a solid is obtained which is only partially soluble in either dilute acids or alkaline sulphides and which varies in color from an orange-yellow when rich in stannic sulphide through a bright red to a very dark red when rich in

thallium sulphide. Loczka[1] in 1898 mentioned this peculiar precipitate and promised to tell more about it; but nothing has appeared since, so we ventured to take up the problem. This could have been worked out by the same method as the preceding, using a solution of an alkaline sulphide as solvent, with thallium sulphide and stannic sulphide as the other two components, and determining the dissolved tin for varying compositions of the precipitate. On account of the striking differences of color it was thought that the point at which there was a change in the solid phase could be determined more readily by the microscope. This method was tried with the following results: over the range of concentrations from pure Tl_2S to a point corresponding to the composition Tl_4SnS_4, there were distinguishable two phases, a black and a red, both with a tendency toward crystalline structure and both opaque; at the point $2Tl_2S.SnS_2$ only one phase was present, the red crystalline opaque phase. From this point to 76 molecular percent SnS_2, two phases were present, the red crystalline opaque phase and an orange-yellow amorphous translucent phase; from 76 percent SnS_2 to pure SnS_2, the solid is entirely homogeneous and changes gradually in color from orange-yellow to the light yellow of pure SnS_2. These observations show that besides the pure components two other phases are present in the series, a compound Tl_4SnS_4 and a series of solid solutions running from 76 percent SnS_2 to pure SnS_2. Another indication of the formation of the compound Tl_4SnS_4 is noticed when precipitates containing an excess of SnS_2 are treated with sodium sulphide solution. Stannic sulphide will be dissolved until the residue has the composition Tl_4SnS_4 and then no more will be dissolved even on increasing the concentration of Na_2S to four mols. per liter and boiling. The compound Tl_4SnS_4 is decomposed, however, by a boiling solution of sodium sulphide when the concentration of the latter is about five mols. per liter.

The similar insoluble precipitates formed with arsenic

[1] Chem. Centralblatt, (5) 2 I, 657 (1898).

and antimony sulphides and with stannous sulphide are now under investigation.

The results of this paper are as follows:

1. A general method has been described for determining the phases in mixtures of two insoluble salts.

2. An application of the method to mixtures of lead oxide and lead carbonate shows that white lead is a definite compound having the formula $PbO_2H_2.2PbCO_3$.

3. A colorimetric method has been used with mixtures of thallous and stannic sulphides. The solid phases are Tl_2S, Tl_4SnS_4, and a solid solution running from 76 to 100 molecular percents of SnS_2.

This work was suggested by Professor Bancroft and has been carried on under his direction.

Cornell University.

THE FLOW OF LIQUIDS THROUGH CAPILLARY SPACES[1]

BY J. M. BELL AND F. K. CAMERON

MOVEMENT OF LIQUIDS THROUGH CAPILLARY TUBES

In a former publication[2] an empirical equation was proposed to describe the movement of water and of aqueous solutions through such media as blotting-paper and soils. This equation is

$$y^n = Kt, \qquad (1)$$

where y represents the distance through which the liquid has moved in the time t, and n and K are constants depending on the temperature and the specific substances.

Theoretical Discussion.—The movement of a liquid from one level to another through a capillary tube has been studied by Poiseuille.[3] In his experiments the ends of the capillary tube opened into large reservoirs, and the length of the capillary tube through which the liquid passed was constant. The results show that the amount of water which passes through the tube in a given time is proportional to the difference in level between the liquid in the two reservoirs, proportional to the fourth power of the diameter of the tube, and inversely proportional to the length of the tube, provided the length is very long in comparison with the diameter. This is expressed by the equation

$$Q = C\frac{HD^4}{L}, \qquad (2)$$

where Q is the amount of liquid which passes through in unit time, H is the difference in level or "head," D and L are the diameter and length of the capillary tube respectively, and C is a constant. This formula may be applied to the advance

[1] Published by permission of the Secretary of Agriculture.

[2] Bull. No. 30, Bureau of Soils, U. S. Department of Agriculture (1905).

[3] Ann. Chim. Phys. (3) 7, 50 (1843).

or retreat of water in a capillary tube, only when the assumption be made that the energy gained or lost with change of velocity is negligible in comparison with the energy gained or lost in the change of level of the water or in the friction against the walls of the tube.

For a constant difference in level and for a tube of uniform bore, equation (2) may be simplified to the form

$$Q = \frac{C}{L}, \tag{3}$$

Now, the amount of water which passes through the tube in unit time is a measure of the velocity, and if we are measuring the advance or retreat of a liquid, we may write $\frac{dL}{dt}$ instead of Q and equation (3) becomes

$$\frac{dL}{dt} = \frac{K}{L}, \tag{4}$$

which, when integrated between the limits L_1, L_2, becomes

$$L_2^2 - L_1^2 = K(t_2 - t_1). \tag{5}$$

Returning now to equation (1), when $n=2$, the equation becomes

$$y^2 = Kt, \tag{6}$$

and if y_1, t_1 and y_2, t_2 be corresponding values of the variables, we obtain

$$y_2^2 - y_1^2 = K(t_2 - t_1), \tag{7}$$

which is identical with equation (5).

In equation (5) the constant K being proportional to C_1 of equation (3) varies directly as the difference in level or "head," and directly as the fourth power of the diameter of the tube.

Experiments.—Capillary tubes of about 1 mm diameter were laid on a millimeter scale on a horizontal table. A length of about 10 or 12 cm of the tube was bent down over the end of the table and this end dipped into the liquid. The tube was filled with the liquid by applying suction at the open end and the rate of retreat of the liquid was observed.

The value of the quantity H of equation (2) may be found from the difference in level between the horizontal capillary tube and the natural position of the liquid in the capillary tube, which in the case of water, alcohol or benzene will be considerably above the free surface of the liquid into which the tube dips. The quantity L is the length of the capillary tube filled with liquid, including, of course, the vertical part of the tube. In the following tables x is the length of the horizontal part of the thread, l is the length of the vertical portion of the tube and t is the time taken for the liquid to move to any given point of the tube.

Equation (5) becomes

$$(x_2 + l)^2 - (x_1 + l)^2 = K(t_2 - t_1). \qquad (8)$$

The following tables give the results of several experiments upon the movement of water, alcohol, or benzene. In these tables K has been calculated from the above formula (8),

$$K = \frac{(x_2 + l)^2 - (x_1 + l)^2}{t_2 - t_1}.$$

The values x_1, t_1, are taken from the table. The temperature did not vary over 0.2° C during any experiment.

Discussion of Results.—There are several sources of error in the results which have been obtained in the above manner. Where the value of x is small and consequently the velocity of retreat of the liquid is great, the possible error of reading is somewhat large. The tube may not have been absolutely uniform in bore over its whole length, and as the amount of liquid which passes through a tube is proportional to the fourth power of the diameter, very small variations in the diameter will have large effects on the velocity of flow. The surface tension of the liquid changes with the change of velocity and it is possible that this change may have had an appreciable influence on the results. Another source of error is involved in an assumption in the original deduction of the formula, *viz.*, that the changing velocity or acceleration of a liquid flowing through the tube is negligible in comparison

TABLE I.

Water, $l = 9.0$ $x_1 = 114.3$ $t_1 = 370$

Time, t Seconds	Distance, x obs. cm	Distance, x Calc. (K = 40.9) cm	$K = \frac{(x+9)^2 - (123.3)^2}{t - 370}$
0	0.0	0	40.9
10	13.0	13.0	40.9
20	21.0	21.0	40.9
35	29.0	29.6	41.1
50	36.2	37.0	41.1
70	44.8	45.2	41.0
100	54.9	55.5	41.2
130	64.3	64.3	40.9
160	72.0	71.7	41.1
190	79.6	79.6	40.9
220	85.9	86.3	41.3
250	92.3	92.5	41.2
280	97.8	98.4	42.1
310	103.7	103.9	41.8
340	108.8	109.2	44.1
370	114.3	—	—
400	119.2	119.2	41.2
430	124.6	123.9	38.6
460	128.8	128.4	42.2
520	138.0	137.1	42.7

TABLE II

Water, $l = 10.0$, $x_1 = 140.0$, $t_1 = 370.0$

Time, t Seconds	Distance, x obs. cm	Distance x Calc. (K = 60.5) cm	$K = \frac{150^2 - (x+10)^2}{370 - t}$
0	0.0	1.4	59.8
10	16.5	16.9	59.9
20	26.2	26.3	59.9
30	33.4	33.9	60.0
40	39.3	40.3	60.2
55	48.9	48.7	60.0
70	56.3	55.9	59.8
100	68.4	68.5	60.0
130	79.4	79.3	59.9
160	88.3	89.0	60.6
190	97.2	97.8	60 7
220	105.0	106.0	61.4
250	112.9	113.4	61.2
280	119.8	120.6	62.3
310	126.9	127.4	60.5
340	133.4	134.1	64.1
370	140.0	—	—

TABLE III

Alcohol, $l = 7.0$, $x_1 = 130.5$, $t_1 = 270$

Time t Seconds	Distance, x obs. cm	Distance, x Calc. (K = 69.8) cm	$K = \frac{137.5^2 - (x+7)^2}{270 - t}$
0	0.0	0.0	69.8
10	20.3	20.5	69.8
20	31.8	31.1	69.6
30	39.7	39.4	70.1
45	49.5	49.6	69.8
60	57.4	58.2	70.3
75	65.8	65.8	69.8
90	72.8	72.7	69.7
105	78.8	78.9	70.0
120	84.7	84.8	70.0
150	96.0	95.6	69.1
180	105.3	105.4	69.9
210	114.4	114.3	69.5
240	122.3	122.7	72.9
270	130.5	—	—

TABLE IV

Benzene, $l = 12.0$, $x_1 = 128$, $t_1 = 147$

Time, t Seconds	Distance, x obs. cm	Distance, x Calc. (K = 133.1) cm	$K = \frac{140^2 - (x+12)^2}{147 - t}$
0	0.0	0.0	133.1
2	10.0	5.3	131.8
12	30.0	28.4	132.1
22	43.0	42.4	132.6
32	53.3	53.5	133.3
42	62.6	63.0	133.7
52	72.0	71.4	132.0
62	80.0	79.0	131.0
72	87.0	85.0	130.6
82	93.2	92.8	131.3
92	98.8	98.8	133.1
102	104.4	105.5	134.4
112	110.2	110.2	133.4
122	115.7	115.6	131.7
132	120.7	120.7	132.7
147	128.0	—	—

with the other forces at work, *viz.*, the surface tension, the friction, and the "head."

In spite of all these sources of error the results are well described by the equation derived from Poiseuille's formula.

MOVEMENT OF LIQUIDS THROUGH POROUS MEDIA

It is not possible to measure the rate of movement of a liquid through porous substances such as blotting-paper and soils in the same manner as this movement through capillary tubes has been measured. In the case of a liquid running into a clean glass tube, the glass becomes wet in advance of the main body of liquid, and there is also the same phenomenon in the case of porous material. In this latter case, however, there is no way of distinguishing between that portion of the substance which is merely wet by a capillary film of liquid over the grains or fibers, and that portion of the substance whose interstices are filled with liquid. In the following experiments the distance which had become wet by the liquid was read at various times. Strips of blotting-paper were cut 3 cm wide and about 20 cm long and then scaled by marking with a pencil. At the beginning of the experiment one end of the paper was immersed in the liquid. In the case of the soils, tubes of 1 cm diameter were filled with dry soil and were packed as nearly as possible in the same way by tapping the end of the tube. At the beginning of the experiment the tubes were lowered to touch the surface of the liquid. No precaution was taken to preserve a constant temperature, but temperature readings did not vary more than 0.2° C during any experiment. The effect of gravity is negligible in these cases for the same results have been obtained when the paper is held in a horizontal position as when it stands in a vertical position. The capillary forces are much greater than the gravitational forces where the distance to which the water has risen is small in comparison with the distance to which it may ultimately rise.

The following tables give the results of experiments upon the rate of flow of water and of a solution of potassium chloride

through blotting-paper and upon the rate of flow of water through columns of dry soil. The columns of the tables headed by "K" give the values of this constant calculated from the equation

$$y^n = Kt.$$

The value of n was found graphically. Taking logarithms of both sides of this equation we have

$$n \log y = \log K + \log t,$$

and when $\log y$ and $\log t$ are plotted, all the points are found to lie on a straight line, showing that the original equation describes the facts accurately. It will be observed that the slope of this line is n and that one of the intercepts is log K.

TABLE V

Distilled water in blotting-paper

Time, t Min.	Height, y cm	K ($n = 2.3$)
0.0	0.0	—
0.25	1.51	10.4
0.5	2.29	—
0.75	2.41	10.2
1.0	2.72	10.2
1.25	2.97	10.0
1.5	3.20	9.9
1.75	3.44	10.1
2.0	3.59	9.7
2.5	3.95	9.7
3	4.28	9.7
4	4.87	10.0
5	5.39	10.0
7	6.28	10.1
10	7.33	10.1
13	8.11	9.9
20	9.85	10.1
25	10.8	10.1
30	11.6	10.0
40	13.1	9.8
50	14.2	9.4
60	15.4	9.5

TABLE VI

Potassium chloride solution in blotting-paper.

Time, t Min.	Height, y cm	K ($n = 2.35$)
0	0	—
0.25	1.41	9.0
0.5	2.05	8.6
0.75	2.40	10.4
1	2.77	11.0
1.5	3.33	11.3
2	3.74	11.1
3	4.54	11.7
4	5.13	11.7
5	5.69	11.8
7	6.52	11.2
10	7.62	11.8
13	8.46	11.6
16	9.23	11.6
20	10.2	11.8
25	11.3	11.9
30	11.8	10.9

TABLE VII

Distilled water in columns of Penn loam soil (T = 18°)

Time, t Min.	Height, y cm	K ($n = 2.05$)
0	0	—
1	0.77	0.58
2	1.15	0.66
3	1.58	0.85
4	1.87	0.90
5	2.29	1.10
7	2.56	0.97
10	2.95	0.92
15	3.64	0.94
20	4.15	0.93
30	5.03	0.93
40	5.96	0.97
50	6.59	0.96
60	7.18	0.95
75	7.90	0.93
90	8.69	0.94
105	9.29	0.92

TABLE VIII
Distilled water in Penn loam soil (T = 21°)

Time, t Min.	Height, y cm	K ($n = 2.25$)
0	0	—
1	1.15	1.37
2	1.54	1.33
3	1.85	1.33
4	2.08	1.30
5	2.28	1.28
7	2.59	1.21
10	2.97	1.16
15	3.47	1.10
20	3.90	1.07
30	4.67	1.06
40	5.39	1.11
50	5.90	1.09
60	6.47	1.12
75	7.20	1.13
90	8.03	1.21
105	8.72	1.25

The values of K in these tables are constant within the errors of experiment, and consequently the formula proposed is accurate within the limits of the experimental errors.

In the following table there have been calculated the results of Loughridge[1] upon the passage of water through an alluvial soil from the Gila River. The figures have been taken from a diagram and are therefore approximate only.

TABLE IX
Alluvial Soil, Gila River

Time, t Min.	Height, y Inches	K ($n = 1.86$)
2	1.5	1.05
5	2.4	1.02
10	3.6	1.08
15	4.3	1.01
30	6.3	1.05
60	9.2	1.07

[1] Report Agr. Exp. Stat. Univ. California, 1893-94, p. 93.

After 125 days water rose in this soil to a height of 47 inches. Other results have been given in tabular form in the same paper but it is not possible to obtain from the diagram sufficiently close approximations to the figures, to test the formula. In the majority of cases described in the literature the times of observations are so long, and the heights observed are so great that gravitational and possibly other effects are introduced, which materially alter the results, and consequently the formula does not hold for such cases. It does not seem worth while to cite further cases in illustration of the formula, as the specific data do not in themselves possess any special value in this connection.

SEPARATIONS BY ABSORBING MEDIA

When a solution passes through a porous material there is very often a separation effected, either of different solutes from each other, or the solution into some of the pure solvent and a stronger solution, or both effects may be superimposed. The separation of a solution into some of the pure solvent and a stronger solution has been observed by J. J. Thomson[1] in the case of potassium permanganate solution rising through filter-paper. The paper is wet by the solvent, water, for a considerable distance in advance of the color produced by the permanganate. Trey[2] has observed that when a solution containing copper and cadmium salts is allowed to run into filter-paper, the cadmium salt moves faster than the copper and thus a partial separation is effected. Goppelsröder[3] has taken advantage of the different absorptive power of paper for different dyes and has succeeded in separating a rose-red colored substance, probably fuchsine, from commercial azuline, the azuline thereby losing its violet tint and acquiring a purer blue color.

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[1] Applications of Dynamics to Physics and Chemistry, 1888, p. 191.

[2] Zeit. anal. Chem. 37, 743 (1898).

[3] Verhandlung d. Naturforsch. Ges. in Basel, 3, 263 (1861-63); Mitteil. d. techn. Gewerbemuseums, Wien (1889).

The separation of solute and solvent has been made a velocity study and here two rates have been measured, the rate at which the paper becomes wet and the rate of the movement of the colored solution through the paper, and some experiments have been made upon the rate of absorption of solutions of eosine by blotting-paper.

TABLE X

Sodium eosine solution in blotting-paper

Solution containing 5.82 grams per liter

Time Min.	Height Wet cm	K ($n = 2.2$)	Height Colored cm	K ($n = 2.2$)
0	0	—	0	—
0.25	1.28	6.9	1.08	—
0.5	1.72	6.6	1.41	4.3
0.75	2.15	7.2	1.67	4.1
1	2.54	7.7	1.92	4.2
1.5	2.97	7.3	2.44	4.7
2	3.36	7.3	2.69	4.4
2.5	3.74	7.3	2.97	4.4
3	4.05	7.2	3.23	4.4
4	4.59	7.1	3.69	4.4
5	5.10	7.2	4.10	4.5
7	6.03	7.4	4.75	4.4
10	7.05	7.3	5.54	4.3
20	9.54	7.1	7.62	4.4
25	10.4	6.9	8.87	4.8
40	12.6	6.6	9.98	4.0

In Figure 1, Curve 1 shows the height to which pure water rose at different times. Curve 2*a* shows the height which had become wet, and Curve 2*b* shows the height which was reddened. The original solution in this case contained 5.82 grams per liter. A strip of paper was dipped into a solution containing twice the amount of the dye per liter. Curve 3*a* represents the rate at which the paper became wet and Curve 3*b* the rate at which it became red.

It will be seen from the curves that the rate at which water travels is decreased by the presence of sodium eosine, that the greater the concentration the less is the rate, and that

TABLE XI

Sodium eosine solution in blotting-paper

Solution containing 11.64 grams per liter

Time Min.	Height Wet cm	K ($n = 2.25$)	Height Colored cm	K ($n = 2.35$)
0	0	—	0	—
0.25	1.18	5.8	1.05	4.6
0.5	1.69	6.5	1.51	5.3
0.75	2.03	6.6	1.80	5.3
1.0	2.28	6.4	2.08	5.6
1.5	2.80	6.8	2.44	5.4
2.0	3.10	6.4	2.72	5.3
2.5	3.49	6.7	2.97	5.2
3	3.85	6.9	3.26	5.4
4	4.26	6.5	3.69	5.3
5	4.75	6.7	4.00	5.2
7	5.54	6.7	4.64	5.3
10	6.46	6.6	5.39	5.3
13	7.31	6.8	6.10	5.4
16	8.03	6.8	6.64	5.3
20	8.85	6.8	7.28	5.3
25	9.67	6.6	8.11	5.5
30	10.5	6.6	8.67	5.3
40	11.7	6.3	9.75	5.3

the separation of water and eosine is more marked for the lower concentration.

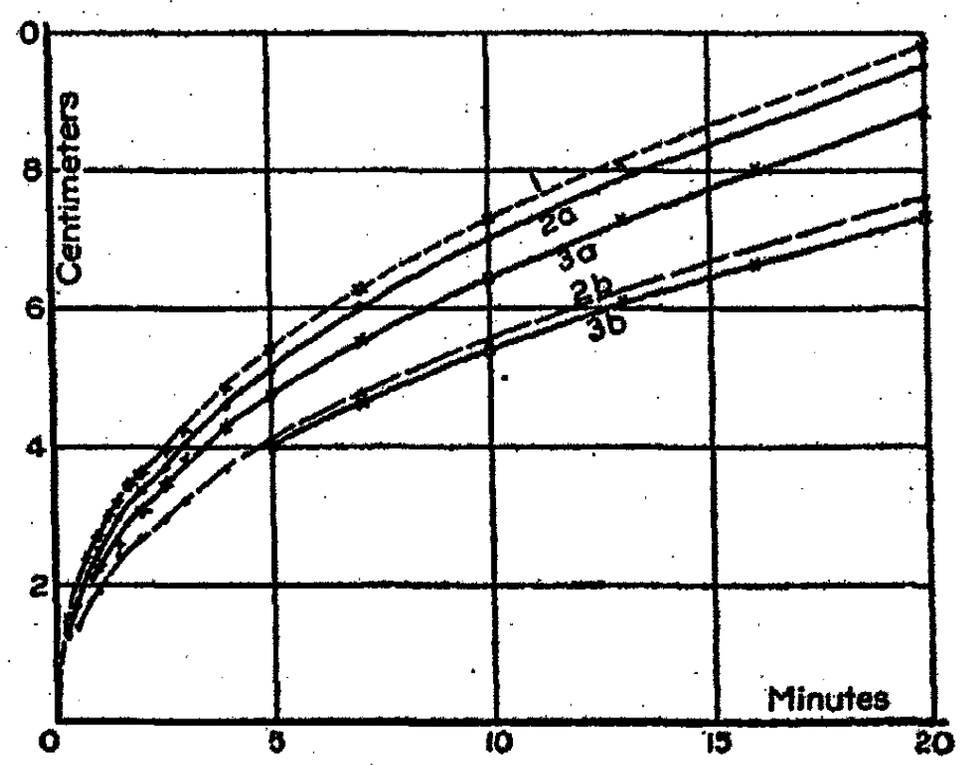


Fig. 1

The effect of potassium chloride on the rate at which sodium eosine is absorbed was determined at 25° C, and the results given in Tables VI and XII are plotted in Figure 2.

TABLE XII

Solution containing sodium eosine and potassium chloride in blotting paper. Solution containing 50 grams KCl and 5.83 grams sodium eosine per liter

Time Min.	Height Wet cm	K ($n = 2.3$)	Height Colored cm	K ($n = 2.9$)
0	0	—	0	—
0.5	1.80	7.6	0.77	0.94
1.0	2.56	7.9	1.03	1.09
1.5	3.08	8.9	1.28	1.36
2	3.51	8.9	1.41	1.35
3	4.28	9.4	1.67	1.48
4	4.87	9.5	1.80	1.37
5	5.39	9.7	2.05	1.61
7	6.23	9.6	2.39	1.78
10	7.23	9.5	2.56	1.52
13	8.08	9.4	2.69	1.36
16	8.87	9.3	2.87	1.33
20	9.61	9.2	3.08	1.31
25	10.51	9.0	3.33	1.31
30	11.5	9.2	3.54	1.30
40	13.3	9.6	3.98	1.37

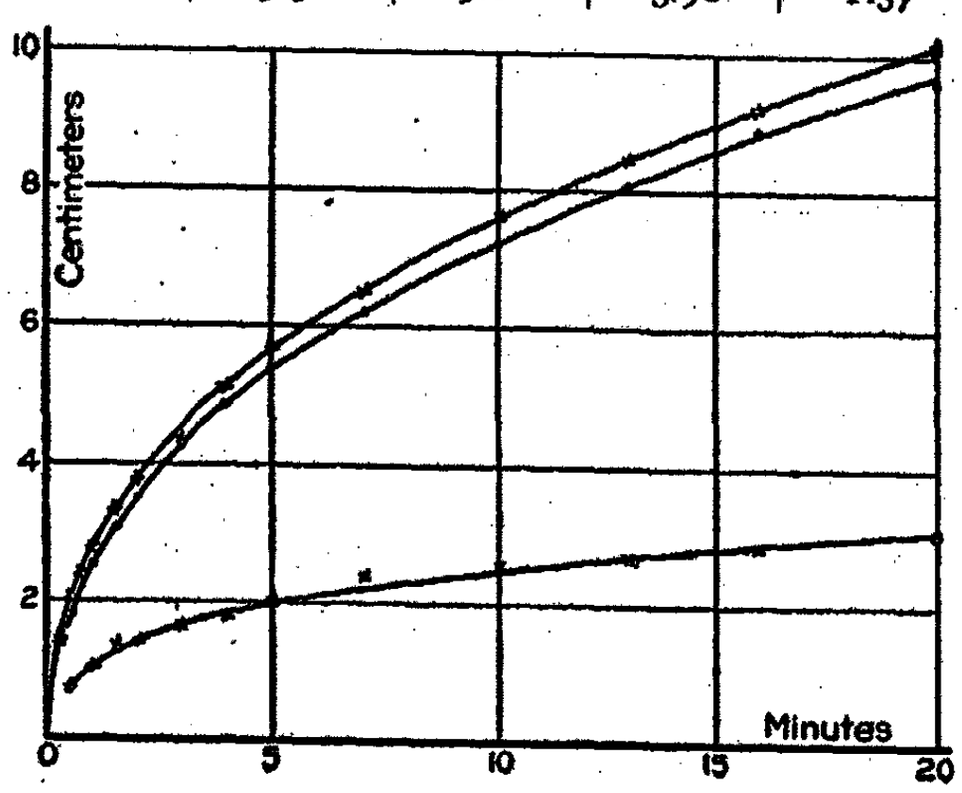


Fig. 2

It is quite evident that the effect of the potassium chloride is to decrease markedly the rate at which the dye travels through the paper. We have thus shown that the solutes do not act independently of one another, but the nature and extent of this dependence have yet to be determined.

The rate at which certain dye solutions rise in columns of dry soil has been measured and the general results are quite similar to those obtained for the rise of such solutions through paper. Two dyes were first tried which were markedly absorbed by paper, that is, the color rose only a small distance through the paper.

TABLE XIII

Dye solution in columns of Penn loam soil (T = 18°)

Time Min.	Height wet by safranine solution containing 2 grams per liter cm	K ($n = 2.05$)	Height wet by methylene blue solution containing 2 grams per liter cm	K ($n = 2.05$)
0	0	—	0	—
1	0.90	0.80	0.90	0.80
2	1.28	0.82	1.54	1.21
3	1.67	0.95	1.87	1.21
4	1.92	0.95	2.13	1.18
5	2.13	0.94	2.26	1.07
7	2.44	0.89	2.69	1.09
10	2.82	0.94	3.20	1.08
15	3.41	0.83	3.98	1.13
20	3.93	0.83	4.70	1.19
30	4.67	0.80	5.51	1.12
40	5.51	0.83	6.39	1.12
50	6.03	0.80	6.98	1.08
60	6.67	0.82	7.59	1.06
75	7.36	0.80	8.74	1.14
90	8.03	0.80	9.05	1.02
105	8.85	0.83	9.67	1.00
120	9.36	0.83	10.0	0.94

It will be observed that the dyes moved into the soils too slowly for any measurements and that the rate at which distilled water rose was intermediate between the rates at which the soils became moist from the two dye solutions. These differences are, however, not great enough to draw any

general conclusions, for they might be attributed to slight differences in the packing of the soil in the tubes.

Two other dyes were tried, coralline and indigo carmine, which move through paper rather readily. It was found very difficult to read the height to which the dye had risen because it rose to a considerable height on one side of the tube and would scarcely rise at all on the other side, in some cases the difference being as great as 4 cm. However, a rough estimate was made of the average height of the dye in the tube when viewed from all directions. It was not found so difficult to measure the height to which the water rose, for in this case the differences of level were never more than 1 cm. The following results were obtained for the same kind of soil as before, Penn loam, and at the same time the rate at which coralline rose in Podunk fine sandy loam was measured. The temperature was 21° C.

TABLE XIV

Indigo carmine in Penn loam soil (T = 21°)

Solution containing 2 grams per liter

Time Min.	Height Wet cm	K ($n = 2.25$)	Height Colored cm.	K ($n = 2.25$)
0	0	—	0	—
1	1.28	1.75	0.64	0.37
2	1.67	1.59	0.90	0.39
3	2.05	1.68	—	—
4	2.26	1.56	—	—
5	2.49	1.56	1.02	0.21
7	2.74	1.38	—	—
10	3.20	1.40	—	—
15	3.72	1.29	—	—
20	4.28	1.32	1.92	0.22
30	5.10	1.31	—	—
40	5.77	1.29	2.69	0.23
50	6.41	1.26	3.20	0.28
60	6.90	1.29	—	—
75	7.46	1.23	—	—
90	8.74	1.46	3.59	0.20
105	9.00	1.33	—	—

TABLE XV

Coralline solution in Penn loam soil (T = 21°)

Solution containing 2 grams per liter

Time Min	Height Wet cm	K ($n = 2.25$)	Height Colored cm	K ($n = 2.25$)
0	0	—	0	—
1	1.02	1.05	—	—
2	1.36	1.00	—	—
3	1.61	0.98	—	—
4	1.92	1.08	—	—
5	2.10	1.06	—	—
7	2.39	1.01	—	—
10	2.74	0.98	—	—
15	3.49	1.11	—	—
20	4.05	1.16	—	—
30	4.67	1.07	0.51	0.007
40	5.46	1.14	0.69	0.011
50	6.06	1.15	—	—
60	6.62	1.17	0.77	0.009
75	7.10	1.10	—	—
90	8.00	1.20	0.90	0.009
105	8.46	1.16	—	—

TABLE XVI

Coralline solution in Podunk fine sandy loam (T = 21°)

Solution containing 2 grams per liter

Time Min.	Height Wet cm	K ($n = 2.05$)	Height Colored cm
0.0	0	—	—
0.5	3.46	25.5	—
1.0	5.03	27.5	—
1.5	6.41	30.2	—
2	7.44	30.7	1.54
3	9.00	30.2	—
4	10.5	31.0	—
5	11.6	29.6	2.31
7	13.6	30.2	—
10	15.9	29.0	2.56
15	19.0	28.0	2.74
20	21.2	26.2	—
25	23.0	24.8	3.08

The above tables indicate that the same empirical formula will describe the rate of flow when a solution is used which undergoes a change while moving through the medium. Both the measurable heights, *viz.*, the height wet by the solvent and the height colored by the dye, when plotted against the time, give the same kind of parabolic curves. In all these cases the value of n lies above 2 which is the value of n when a liquid is moving through a capillary tube.

Conclusion

In this paper it has been shown that:

1. The movement of water through a capillary tube is accurately described by the equation $y^2 = Kt$, an equation derivable from Poiseuille's equation by making the assumption that the acceleration is negligible in comparison with the velocity. The same restrictions regarding the size of the tube hold in this case as in Poiseuille's experiments, *viz.*, the length of the tube must be great as compared with the diameter.

2. An empirical equation, $y^n = Kt$, describes the movement of water and solutions through porous materials, such as filter-paper and dry soils. The value of n lies above 2 in most cases.

3. The empirical equation, $y^n = Kt$, describes the movement through soils and paper, of solutions which suffer change during the process. Both the advance of the solute and of water in the medium are described by the formula.

Bureau of Soils,
U. S. Department of Agriculture,
Washington, D. C.

NEW BOOKS

Systematische Durchführung thermochemischer Untersuchungen. *Zahlenwerte und theoretische Ergebnisse. By Julius Thomsen. Autorisierte Übersetzung von J. Traube. 16 × 25 cm; pp. viii + 382. Stuttgart: Ferdinand Enke, 1906. Price: paper, 12 marks.*—By omitting details as to experimental work and by condensing wherever possible, the author has succeeded in giving in one volume the essential data from the larger four-volume work. It is now possible for every chemist to have Thomsen's data at hand in his own library. As everybody knows, the work of Thomsen has two points in its favor which are of great importance. In the first place the ground has been covered systematically, and in the second place the experiments have all been made by one man. While this latter fact does not ensure absolute accuracy by any means, it does guarantee that the measurements by the same method are comparable.

The data are presented under four heads: formation and properties of aqueous solutions; heat effects for compounds of the metalloids; compounds of metals with metalloids; organic compounds.

In the discussion of the results, the author has confined himself almost exclusively to the results themselves. We thus get a theoretical treatment based solely on thermochemical data. This is very interesting, but it has its disadvantages. The author is not able to check his results by reference to work along other lines and he is often compelled to leave points unexplained which have already been cleared up. His data for the hydration for sodium sulphate, p. 27, point definitely to the existence of the monohydrate, a salt which was supposed to be formed when the decahydrate effloresced. It is now known that this is not the case. Either Thomsen's determination is in error by 20–25 percent or we have an adsorption phenomenon with the anhydrous salt. If we make the latter, rather improbable, assumption, it vitiates the conclusions to be drawn from the behavior of other anhydrous salts. If we accept the hypothesis of experimental error, we have no guarantee as to the accuracy of the other measurements on hydration.

Quite apart from this difficulty, the whole discussion of heats of hydration would have been more valuable if parallel references had been made to the pressure relations.

The heats of neutralization of acids by bases certainly call for a reference to the electrolytic dissociation theory and the relation between the avidity constant of Thomsen and the affinity constant of Ostwald seems worth mentioning. If the author had kept this relation in mind, he would not have made the sweeping and erroneous statement that the avidity is independent of the concentration between N/100 and N/400.

If the author had kept in touch with other work, he would have known that the variation of the heat of oxidation of amorphous phosphorus with the methods of preparation of the phosphorus, p. 167, was a most gratifying proof of the fact that we have hysteresis phenomena with amorphous phosphorus and that there are several, perhaps many, forms of red phosphorus.

It would also have been better to have made use of the free energy conception instead of that of total heat effect. If thermochemists would only realize it, it is through their work that we shall get quantitative measurements of free energy in most cases. We need measurements on heats of reaction as they vary with the temperature.

As a collection of data the book is of great value to every chemist. It will also be interesting to many as a document, because it shows what can and what cannot be done by an exceptionally able man who has chosen deliberately to ignore all work but his own. Even the thermochemical work of others is passed by. To a certain extent one can understand that in the case of Berthelot, but Stohmann's measurements were quite as accurate as those of Thomsen. The book is a self-contained whole, both as to the experimental and the theoretical side. We must admire the consistency with which the author's policy has been carried out, while reserving the right to question the wisdom of the policy.

Wilder D. Bancroft

Die Elektrolyse geschmolzener Salze. *Dritter Teil: Elektromotorische Kräfte. By Richard Lorenz. (Monographien über angewandte Elektrochemie, XXII. Band.) 17 × 24 cm; pp. xviii + 322. Halle: Wilhelm Knapp, 1906. Price: paper, 10 marks.*—This third and last volume on the electrolysis of fused salts deals with electromotive forces and with polarization phenomena. The subject is classified under three heads: polarization; cells; electromotive force and heat of reaction. The book is an admirable one and will be invaluable as a work of reference. The author appreciates that from a theoretical point of view the fused salt is the simplest possible case, because there is no solvent. If one is to assume electrolytic dissociation in an aqueous solution, there seems to be no justification for not assuming electrolytic dissociation in a fused salt. Since conduction in a solid salt apparently differs in degree only from that in a fused salt, the logical conclusion is that we have electrolytic dissociation in solid salts. This is the conclusion which the author draws and it is one which it seems difficult to avoid drawing if the premises are granted.

One may, however, question the author's conclusion that the cation alone migrates in solids. This is based on Lehmann's experiments with silver iodide and on Warburg's experiments with glass; but it seems to the reviewer that the results obtained were a necessary consequence of the way in which the experiments were carried out and that they therefore do not have the theoretical significance which the author ascribes to them. Lehmann electrolyzed silver iodide between silver electrodes and found that silver was carried from one electrode to the other. If he could have carried on the electrolysis between iodine electrodes, he would have found that iodine was carried from one electrode to the other. It is very important to distinguish between what is difficult experimentally and what is impossible theoretically.

The only slips noticed by the reviewer are the consistent misspelling of Mayer's name and the omission of a reference on p. 186 to the paper in which Richards showed that the electromotive force of a cell is a linear function of the temperature when the heat of reaction is independent of the temperature.

Wilder D. Bancroft.

Lehrbuch der allgemeinen Chemie. *By W. Ostwald. In zwei Bänden. Zweite, umgearbeitete Auflage. Zweiten Bandes, dritter Teil: Verwandtschaftslehre. Zweiter Teil. 16 × 24 cm; pp. 264 Leipzig: Wilhelm Engelmann, 1906. Price: paper, 7 marks.*—The first 216 pages are devoted to solid solutions while the remainder of the number contains the first instalment on adsorption. The author meets the difficulties in regard to the experiments of Küster, Walker and Appleyard, and others by postulating that we are dealing with adsorption phenomena and not with solid solutions whenever absurd results for the molecular weight are obtained from the distribution ratio. This is both frank and ingenious. Whether it is final, is a bit doubtful.

The available material on solid solutions is presented with characteristic thoroughness and clearness. *Wilder D. Bancroft.*

Maschinenkunde für Chemiker. *Ein Lehr- und Handbuch für Studierende und Praktiker. By Albrecht von Ihering. (Handbuch der angewandten physikalischen Chemie, Herausgegeben von Prof. Dr. G. Bredig.) Band III. 16 × 25 cm; pp. ix + 396. Leipzig: Johann Ambrosius Barth, 1906. Price: paper, 14 marks; bound, 15 marks.*—This volume should be of distinct service to chemists. It contains a great deal of information about matters with which the chemist ought to be familiar but of which he is often only too ignorant. The author discusses boilers, steam engines, gas engines, water wheels, pumps, conveyors, crushers, mixers, stills, blast-furnaces, electric furnaces, vacuum pans, ice machines, etc. The book is essentially descriptive and descriptive from an engineer's point of view. Thus there is practically no theory given, p. 342, for the multiple effect evaporators. To this extent the book falls short of being applied physical chemistry. It will, however, be very useful as a book of reference and it may hasten the day when some physical chemist will know enough to write a similar book from the point of view of the chemist.

Wilder D. Bancroft

Lehrbuch der Mathematik für Studierende der Naturwissenschaften und der Technik. *Einführung in die Differential und Integralrechnung und in die analytische Geometrie. By Georg Scheffers. 16 × 24 cm; pp. viii + 680. Leipzig: Veit and Co., 1905. Price: paper, 16 marks.*—This exceedingly well-written book provide students of science or technology with the means of teaching themselves effectively as much higher mathematics as is commonly employed in the physical sciences and their technical applications. Being written for the beginner, it presupposes only a little elementary geometry and the rudiments of algebra. Since the beginner may have forgotten much of his school mathematics, or may have but ill understood it, the preliminary matters that he must know are here taken up afresh, even to the solution of quadratic equations. This is fortunate for him, for these affairs are treated delightfully.

Primarily the subject-matter of the book is elementary analytics and calculus. The author's list of topics is: quantities and functions; differentiation and integration; the logarithmic functions; the exponential functions; the goniometric and cyclometric functions; computation of functions; more than one variable. Matters not commonly used in physics and technology are not

considered, and such things as the polytropic curves formed for gases and vapors and the frequently occurring logarithmic and exponential functions are treated with unusual fullness—and unusual clearness. Everything presented is explained in the most careful and complete fashion, and is illustrated by numerical examples and a wealth of graphic constructions. The explanations are so complete and clear that the whole text can easily be worked through without a teacher. Whoever reads it all attentively will gain a sound comprehension of the content and bearing of the elements of the higher mathematics. The book is an exceedingly able performance, and bids fair to become the standard work for its purpose. An extensive index gives it value as a book of reference.

J. E. Trevor.

Recherches expérimentales sur les Contacts liquides. *By A. M. Chanoz. (Annales de l'Université de Lyon, I., Fascicule 18.) 16 × 25 cm; pp. 99. Paris: Gauthier-Villars, 1906. Price: paper, 5 francs.*—The author has studied the differences of potential between two solutions, the effect of membranes on electromotive force, the electrical phenomena connected with osmosis, and the effect of X-rays on osmosis. The most interesting portion of the work is that on the behavior of membranes. When the two sides of the membrane differ, as with a skin, differences are obtained depending on whether a given side of the membrane is in contact with solution A or solution B. These differences disappear, of course, when the two sides of the membrane are alike, as with parchment paper. It seems probable that the behavior of the membrane depends largely on its greater or less permeability. *Wilder D. Bancroft.*

The Influence of Molecular Constitution upon the Internal Friction of Gases. *By Frederick Malling Pedersen. 15 × 24 cm; pp. v + 59. New York: D. Van Nostrand Company, 1906. Price: paper, $.50.*—This is really a doctor thesis. The author has measured the coefficients of internal friction of eight ethers at 100°. Normal propyl ethers have lower coefficients than the corresponding isopropyl ethers. The molecular volumes calculated from the friction agree fairly well with those obtained by Kopp's rule. *Wilder D. Bancroft.*

The Theory of Determinants in the Historical Order of Development. *By Thomas Muir. Second Edition. 14 × 22 cm; pp. xi + 491. New York: The Macmillan Company, 1906. Price: $5.00.*—This admirable presentation of the early history of the theory of determinants, although primarily intended for the student of mathematics, will interest every intelligent user of the determinant notation. Although Leibnitz was the first to discover the rôle played by determinants in elimination between linear equations, his discovery did not become common property. The first to attract attention to a connected exposition of the theory was Vandermonde, in 1771; and the elements of the subject were practically completed by Cauchy in an exhaustive memoir published in 1812. The details of the whole development are very clearly given in the present volume, often indeed in the words of the individual authors. The history is brought down to 1841, and is divided into two parts, which treat respectively of general determinants and of the growth of special forms. Careful and detailed attention is given to the very interesting and important topic of jacobians. *J. E. Trevor*

THE RATES OF THE REACTIONS IN SOLUTIONS CONTAINING POTASSIUM BROMATE, POTASSIUM IODIDE AND HYDROCHLORIC ACID

BY ROBERT H. CLARK

Among the earliest contributions to the literature of this subject is a paper by W. Ostwald,[1] who studied the reaction between hydrogen iodide and bromate in order to determine the accelerating influence of different acids. The author did not attempt to formulate a satisfactory kinetic equation, but calculated the velocity constant from the bi-molecular formula, and came to the conclusion that, in general, the accelerating influence of the different acids is proportional to their affinity constants,[2] the chief exception being in the case of chromic acid. I have carried out a number of experiments on the action of chromic acid, which will appear in a second communication.

In the same year W. Meyerhoffer[3] and O. Burchard,[4] working independently of each other, investigated the reaction, and both came to the conclusion that the rate could not be represented by the formula of the second order or by any other simple formula. Meyerhoffer ascribed the complications to the influence of the iodine formed by the reaction and proposed the equation $\frac{dx}{dt}=\frac{c\,(a-x)^3}{x}$, but it was shown later by Meyer[5] that this equation is not in agreement with the experiments.

In 1890 Gaetano Magnanini[6] made a great many measurements on the rate of this reaction; he, like Ostwald, studied the influence of different acids and noted that the acceleration caused by hydrochloric, nitric and sulphuric acids is not

[1] Zeit. phys. Chem., 2, 127 (1888).

[2] See however, Zeit. phys. Chem., 19, 599 (1891) and Table IV of the present paper, p. 684.

[3] Ibid., 2, 585 (1888).

[4] Ibid., 2, 796 (1888).

[5] Zeit. phys. Chem., 2, 830 (1888).

[6] Gazz. chim. Ital., 20, 377 (1890).

proportional to their concentrations, but failed to draw any general conclusions.

The next paper on the subject, A. A. Noyes'[1] "Contribution to the Knowledge of the Order of Polymolecular Reactions," contains four series of experiments by W. O. Scott, in which the initial concentrations of potassium bromate and iodide were varied, while in all the acid was present in constant excess. Comparison of the constants of the second and third order in the different series led to the conclusion that "the reaction between hydriodic and bromic acids is of the second order."

In the following year in a paper "On the Catalytic Effect of Hydrion on Polymolecular Reactions"[2] Noyes showed from certain of Magnanini's measurements, that the rate of the reaction between hydrobromic and bromic acids is proportional to the square of the concentration of the hydrion.

In spite of this large amount of work, however, the author of the most recent text-book on chemical kinetics[3] is of the opinion that "the course of the oxidation of hydriodic acid by the oxyacids of the halogens appears to be so intricate that a satisfactory application of the mass law has not yet been made." The measurements of the present paper show definitely the influence of the concentration of each reagent on the rate, and the extent to which the results are affected by the presence of the products of oxidation, *viz.*, iodine and bromide.

Plan of the Experiments

In these measurements, in order to trace the effect of the concentrations of each one of the chemicals separately, I have adopted a plan described by Mr. W. C. Bray[4] under the title "Method of Constant Rates" which consists in choosing the concentrations so that "while the amount of change accomplished in a suitable interval of time is sufficient for the

[1] Zeit. phys. Chem., 18, 118 (1890).
[2] Ibid., 19, 599 (1891).
[3] J. W. Mellor: "Chemical Statics and Dynamics," p. 103 (1904).
[4] Jour. Phys. Chem., 7, 93 (1903).

requirements of an accurate analysis, yet the fractional alteration in the concentrations of the reagents involved is so small that the rate may be treated as practically constant during the interval." Where the reaction has proceeded so far that this assumption could not be made, a correction has been applied for the small changes in concentrations of the reagents involved. In all cases these corrections are comparatively small, the conclusions to be drawn from the experiments being, in general, obvious enough, even without the correction.

Method of Working

Temperature.—All the measurements were made at 30°, this temperature being maintained by a thermostat within one-tenth of a degree.

Calibration.—All the pipettes used were calibrated by weighing the distilled water discharged, thirty seconds being allowed for drainage. The burettes were calibrated as described in "Ostwald's Hand- und Hilfsbuch," p. 103.

Details of an Experiment.—Each measurement contained in the following tables involved the preparation of a new reacting mixture. Portions of the stock solutions used in the measurements were kept in the thermostat in glass-stoppered flasks. The potassium bromate was added to a suitable volume of water in a wide-mouthed half-liter glass-stoppered bottle, while the potassium iodide and hydrochloric acid were pipetted into a large test-tube together with enough water to make up a volume of 80 cc. After pipetting out the solutions they were allowed to stand in the thermostat for five minutes, and then the contents of the test-tube were quickly poured into the bottle and shaken, the exact time of mixing being noted. The total volume of the reacting mixture was always 250 cc. When it was desired to stop the reaction the contents of the bottle were rapidly stirred, 10 cc of a half-saturated ammonium bicarbonate solution were thrown in, and the time was noted. The iodine liberated was then determined with hundredth-normal arsenite.

Stock Solutions

Potassium Bromate.—0.0206 F.[1] made from Merck's potassium bromate and standardized by decomposing a known volume with excess of potassium iodide and hydrochloric acid, adding excess of the solution of ammonium bicarbonate, and titrating against the volumetric sodium arsenite.

Potassium Iodide.—0.9890 F. neutralized (to litmus) by hydriodic acid and standardized gravimetrically with silver.

Potassium Bromide.—2.002 F. neutralized and standardized with silver.

Hydrochloric Acid.—Two solutions 0.9539 F. and 0.9542 F. respectively, by comparison (phenolphthalein) with a freshly prepared volumetric potash solution, which in turn was standardized with potassium bichromate.

Sodium Arsenite.—0.02504 F. As_2O_3 (0.10017 normal) prepared according to Mohr[2] and standardized with dry freshly sublimed iodine.

Iodine.—Approximately decinormal, prepared from freshly sublimed iodine and compared frequently with the sodium arsenite, the accurate titre so found being used in the calculations.

Ammonium Bicarbonate.—A half-saturated solution was kept under carbon dioxide; it was tested from time to time, and not used unless a distinct blue color was obtained by adding one drop of centinormal iodine to a mixture of 250 cc water, 10 cc ammonium bicarbonate, 10 cc potassium iodide and 3 cc starch.

The Starch was prepared fresh daily: 1 gram to the liter.

All these solutions were diluted to one-tenth their concentration to form the "stock solutions" and volumetric solutions referred to in the preceding section.

Explanation of the Tables

The numbers at the head of each table, divided by 100,000, give the gram-formula weights of each reagent initially present

[1] Formula weights per liter.

[2] Chemisch-Anal. Titrirmethode, 9th ed., p. 392.

in the 250 cc of reacting mixture. Under t is given the duration of the oxidation in minutes; under x the iodine liberated, expressed as cubic centimeters of 0.010017 normal arsenite solution; and under x' these values corrected for the falling off in concentration of the reagents.[1] $R_o = \frac{dx}{dt}(x=o)$ is the "initial rate," *i. e.*, the number of cubic centimeters of hundredth-normal iodine liberated per minute in the 250 cc of reacting mixture whose composition is, and remains, that given at the head of the table. Under K is given the "constant of the fourth order" multiplied by 10^{13}.

The experiments of Table I are the standard with which are compared those of Tables II, III and IV where the concentrations of the bromate, iodide and acid respectively are doubled.

Effect of Bromate, Iodide and Acid

TABLE I

$KBrO_3$, 20.5; KI, 98.67; HCl, 95.15

t	x	x'	$R_o \times 10^4$	$K \times 10^{13}$
5	0.23	0.231	462	99
10	0.45	0.454	454	97
20	0.89	0.907	453	100
30	1.40	1.44	480	103
45	2.15	2.25	500	104
60	2.80	2.99	498	103
90	4.15	4.56	506	104

Average value, $R_o = 481 \times 10^{-4}$

TABLE II

$KBrO_3$, 41; KI, 98.67; HCl, 95.15

t	x	x'	$R_o \times 10^4$	$K \times 10^{13}$
5	0.46	0.464	928	99
10	0.90	0.907	907	97
20	1.80	1.87	935	100
30	2.75	2.90	966	103
45	4.00	4.32	960	104
60	5.24	5 79	965	103
90	7.60	8.77	973	104

Average value, $R_o = 948 \times 10^{-4}$

[1] See pages 681 and 685.

TABLE III

$KBrO_3$, 20.5; KI, 197.3; HCl, 95.15

t	x	x'	$R_0 \times 10^4$	$K \times 10^{13}$
5	0.45	0.454	908	97
10	0.90	0.915	915	98
20	1.80	1.86	930	99
30	2.75	2.88	960	102
45	3.99	4.30	955	102
60	5.22	5.73	955	102
90	7.53	8.66	962	102

Average value, $R_0 = 936 \times 10^{-4}$

TABLE IV

$KBrO_3$, 20.5; KI, 98.67; HCl, 190.3

t	x	x'	$R_0 \times 10^4$	$K \times 10^{13}$
5	0.92	0.934	1860	100
10	1.85	1.91	1910	102
20	3.62	3.74	1870	100
30	5.39	5.91	1970	105
45	7.75	8.87	1970	105
60	9.76	11.60	1930	102
90	13.93	18.01	2000	106

Average value, $R_0 = 1930 \times 10^{-4}$

Effect of Chlorion and of Atmospheric Oxygen on the Rate

In order to assure myself that the effect of the hydrochloric acid was due entirely to the concentration of the hydrion I made some measurements in which the concentration of the chlorion was doubled by adding sodium chloride. The rate was the same as in the absence of the salt. The addition of very large quantities of potassium chloride, however, retards the oxidation, see Tables IX and X and p. 688.

To find whether the results were affected by access of air,[1] I made some preliminary measurements in duplicate, one of each pair under ordinary conditions, and the other in an atmosphere of carefully purified carbon dioxide.[2] I

[1] Compare Zeit. phys. Chem., 2, 103 (1888), and Gazz. chim. Ital., 20, 382 (1890).

[2] See Dushman: Jour. Phys. Chem., 8 (1904).

failed to detect any difference in the rates in the two cases, and the subsequent measurements were carried out in air.

Effect of the Concentrations of Bromate, Iodide and Acid on the Rate

By comparing Table I with II, III and IV respectively it is readily seen that the velocity of the reaction is proportional to the first power of the concentrations of the bromate and iodide and to the second power of that of the acid, as represented by the equation:

$$\frac{1}{V}\cdot\frac{dx}{dt}=\frac{(A-x)}{V}\frac{(B-x)}{V}\frac{(C-x)^2}{V^3} \qquad (1)$$

This conclusion is confirmed by the constancy of K in the tables as calculated from the integrated form of the above equation:—

$$\frac{KABC^2t}{V^3}=x'=x+\frac{1}{2}\left(\frac{1}{A}+\frac{1}{B}+\frac{2}{C}\right)x^2+\frac{1}{3}\left(\frac{1}{A}+\frac{1}{B}+\frac{3}{C}+\frac{1}{AB}+\frac{2}{AC}+\frac{2}{BC}\right)x^3 \qquad (2)$$

In the tables I have used the symbol x' for the quotient $KABC^2t/V^3$, because it gives the amount of iodine that would be liberated in t minutes if the solution retained its original composition throughout the experiment. The amount of iodine actually liberated, x, is naturally less than x', because of the decrease in concentration of the reagents as the reaction proceeds.

In calculating K the values of A, B and C denoting respectively the initial quantities of $KBrO_3$, KI and HCl have been expressed in the same units as x (see p. 683); thus $A=6KBrO_3$, $B=2/3KI$, $C=HCl$, according to the equation:

$$KBrO_3+9KI+6HCl=3KI_3+KBr+6KCl+3H_2O.$$

For instance in the experiments of Table I, $A=123$, $B=65.78$, $C=95.15$.

In each table the constant increases slightly as the reaction proceeds; no importance can be attached to this fact, however, as a change of from 0.05 to 0.1 cc of the hundredth-normal arsenite used in the analysis would account for the increase.

Effect of Bromide

Judson and Walker[1] have shown that potassium bromide, which is one of the products of the reaction between bromic acid and hydriodic acid, is itself oxidized by bromic acid; this reaction, however, takes place much more slowly than the oxidation of potassium iodide even when equivalent quantities are employed, and in the experiments of Tables I to IV the concentration of the bromide never reached 3 percent of that of the iodide. A few experiments in which small quantities of potassium bromide were added to the reacting mixture gave results identical with those in which no such addition had been made, so that it was not necessary to make any correction for the presence of this product of the reaction.

In this connection a number of experiments were undertaken to see whether the two reactions, *viz.*, the oxidation of potassium iodide and that of potassium bromide by bromic acid, take place independently in the solution. In Tables V and VII potassium bromide alone was present; in those of VI and VIII both bromide and iodide, the latter, however, in comparatively small quantity, as under like conditions the iodide is oxidized 58 times as rapidly as the bromide.

In the fourth column of Tables VI and VIII are entered the sums of the values of x' from Tables I and V, and IV and VII respectively; that is to say, the combined amounts of iodine which would have been liberated in solutions containing the bromide and iodide separately; in each case these sums are greater than the amount of iodine set free in the mixture, as given in column four of Tables VI and VII.

TABLE V

$KBrO_3$, 20.5; KBr, 2000; HCl, 95.15

t	x	x'
20	0.61	0.62
30	0.94	0.95
45	1.42	1.44
60	1.85	1.89
90	2.75	2.86

[1] Jour. Chem. Soc., 73, 411 (1898).

TABLE VI

$KBrO_3$, 20.5; KBr, 2000; KI, 98.67; HCl, 95.15

t	*x*	*x'* (mixture)	*x'* (Sum I and V)
20	1.28	1.31	1.52
30	1.87	1.93	2.39
45	2.75	2.87	3.67
60	3.40	3.58	4.84
90	5.31	5.80	7.82

[Note: As the concentrations of the reagents have the same effect on the rate of oxidation of bromide[1] as on that of iodide, the values of x' in Tables V and VII were calculated from equation (2).

In calculating x' (mixture) for Tables VI and VIII the concentration of the bromide has been regarded as constant, and x' has been computed by means of a modified form of equation (2), *viz.*:

$$x' = x + (1/2A + 1/C)x' + (x-y)^2/2B \qquad (2\ bis)$$

where y is the value of x in Table V, and $x - y$ is substituted for x in the term $x^2/2B$, y being regarded as the iodine liberated (in experiments VI) by the bromine set free by the action of bromate on bromide, and $x - y$ that liberated by direct action of bromate on iodide.]

TABLE VII

$KBrO_3$, 20.5; KBr, 2000; HCl, 190.3

t	*x*	*x'*
20	2.40	2.46
30	3.76	3.91
45	5.39	5.70
60	7.00	7.50
90	9.71	10.71

[1] Judson and Walker: loc. cit.

TABLE VIII

$KBrO_3$, 20.5; KBr, 2000; KI, 98.67; HCl, 190.3

t	x	x' (mixture)	x' (Sum IV and VII)
20	4.75	5.01	6.20
30	7.35	7.98	9.82
45	10.60	12.02	14.57
60	13.40	15.73	19.10
90	18.58	23.43	28.72

The difference between "x' mixture" and "x' sum" in Tables VI and VIII was found to be due to the presence of the large quantities of potassium salts, which, as the readings of Tables IX and X show, retard the oxidation of potassium iodide.

The solutions used in the experiments of these two Tables (IX and X) are the same as those of Tables I and IV, with the addition of enough potassium chloride to make the concentration of the potassium ion the same as in the experiments of Tables V and VII. As is shown in the last columns of Tables IX and X, the iodine liberated in solutions containing both iodide and bromide is the sum of that liberated in solutions containing iodide alone, *plus* the iodine equivalent of the bromide liberated in the absence of iodide. Thus, the two reactions—oxidation of iodide by bromic acid, and oxidation of bromide by bromic acid—proceed independently in the same solution.

TABLE IX

$KBrO_3$, 20.5; KCl, 2000; KI, 98.67; HCl, 95.15

t	x	x'	x' (Sum V and IX)	x' mixture (VI)
20	0.67	0.68	1.30	1.31
30	1.01	1.03	1.97	1.93
45	1.49	1.54	2.96	2.87
60	1.85	1.93	3.78	3.58
90	2.91	3.10	5.85	5.80

TABLE X

$KBrO_3$, 20.5; KCl, 2000; KI, 98.67; HCl, 190.3

t	x	x'	x' (Sum VII and X)	x' from VIII
20	2.65	2.76	5.22	5.01
30	4.00	4.28	8.19	7.98
45	5.85	6.48	12.18	12.02
60	7.39	8.31	15.81	15.73
90	10.79	13.06	23.77	23.43

This simple relation makes it very easy to allow for the effect of the bromide which is formed from the bromate by the action of hydriodic acid. Judson and Walker have shown that the form of the equation for the rate of oxidation of bromide by bromate is the same as that of my equation 1; and the value of its constant calculated from the experiments of Table V, corrected for the high concentration of the potassium ion, and expressed in my units, is 2.2×10^{-13}.

The bromine formed by the oxidation of the bromide would, of course, react instantaneously with the potassium iodide, and liberate an equivalent amount of iodine, so that the total amount of iodine liberated in the time t is governed by the following differential equation, in which D represents the number of equivalents of bromide initially present.

$$\frac{dx}{dt} = (A-x)(C-x)^2\left[100 \times 10^{-13}(B-x) + 2.2 \times 10^{-13}(D+x)\right]V^{-3}. \quad (3)$$

In all the experiments of this paper, except those in which potassium bromide was added at the beginning, D = 0, and the last term of equation (3) may be neglected.

Effect of Iodine

The only other product of the reaction which might influence the rate is iodine. In order to study its effect I undertook the experiments of Table XI in which iodine was dissolved in the stock solution of potassium iodide and its amount determined by titration.

The first column of the table gives the amount of free iodine initially present in the reacting mixture expressed in

cubic centimeters of 0.010017 normal arsenite; the second, under "KI Corr.," the potassium iodide initially present, which was calculated by subtracting one-half the number in the first column from 98.67 (which was the amount of potassium iodide in the solution before addition of iodine), according to the equation:

$$KI + I_2 = KI_3.$$

Under x is entered the amount of iodine liberated during the time t (minutes), obtained by subtracting the initial iodine from the "titration." Under "x calc" is given the amount of iodine that would be liberated in the same time in solutions which contained throughout the experiment the amount of bromate and acid entered at the head of the table, and the amount of potassium iodide entered in the second column under "KI corr.," but no "initial iodine."

It will be noted that the difference between "x" and "x calc." entered in the last column of Table XI, although small, are all positive, and increase with increase in the amount of iodine present. This is in accord with the results of Mr. Dushman's measurements on the rate of oxidation of potassium iodide by iodic acid in the presence of free iodine, and points to the oxidation of triiodion by bromic acid.

The correction for this subsidiary reaction is so small, however, that the relations between concentrations and rate given by equation 2 should hold whether free iodine be present or not, and the equation should be able to account for the whole progress of the reaction between bromic and hydriodic acids from its commencement to its end. This conclusion is borne out by the experiments recorded in Table XLI of the Appendix, for which I am indebted to Mr. F. C. Bowman, where the value of K remains constant within 1 or 2 percent while 95 percent of the bromate is reduced.

Temperature Coefficient

To find the temperature coefficient, I made a series of measurements at 30°, 25° and 0° C.

TABLE XI

$KBrO_3$, 20.5; KI, 98.67; HCl, 190

Initial I	KI corr.	t	Titration	x	x calc.	Diff.
0	98.67	60	9.60	9.60	9.52	0.08
0	98.67	90	13.40	13.40	13.31	0.09
0	98.67	120	16.75	16.75	16.66	0.09
7.73	94.80	60	17.07 17.06	9.33	9.15	0.18
7.73	94.80	90	20.68 20.75	12.98	12.80	0.18
7.73	94.80	120	23.88 23.90	16.16	15.99	0.17
11.75	92.80	60	20.75 20.78	9.01	8.94	0.07
11.75	92.80	90	24.70 24.58	12.89	12.56	0.33
11.75	92.80	120	27.78 27.78	16.03	15.75	0.28
16.78	90.28	60	25.77 —	8.99	8.74	0.24
16.78	90.28	90	29.59 —	12.81	12.32	0.49
16.78	90.28	120	32.43 32.50	15.70	15.38	0.32
20.92	88.21	60	29.88 29.82	8.93	8.60	0.33
20.92	88.21	90	33.51 33.46	12.56	12.07	0.49
20.92	88.21	120	36.60 36.42	15.59	15.16	0.43
40.54	78.40	60	48.26 —	7.72	7.60	0.12
40.54	78.40	90	51.46 51.43	10.91	10.74	0.17
40.54	78.40	120	54.70 54.58	14.10	13.51	0.59
52.40	72.47	60	60.05	7.65	7.13	0.52
52.40	72.47	90	63.09 62.94	10.62	10.02	0.60
52.40	72.47	120	65.98 65.86	13.52	12.66	0.86

TABLE XIII

$KBrO_3$, 20.5; KI, 98.67; HCl, 190.3

At 30°					At 25°					At 0°				
t	x	x'	R	$K.10^{13}$	x	x'	R	$K.10^{13}$	Coeff.	x	x'	R	$K.10^{13}$	Coeff.
20	3.46	3.67	183	98	2.58	2.70	135	72	1.84	0.65	0.66	33	17	—
30	5.10	5.57	185	99	3.81	4.07	136	72	1.85	0.88	0.89	30	16	1.84
45	7.50	8.55	190	101	5.65	6.23	138	74	1.89	1.30	1.33	29	16	1.87
60	9.60	11.39	189	100	7.29	8.28	138	74	1.87	1.75	1.80	30	16	1.85
90	13.40	17.23	191	102	10.37	12.48	139	74	1.89	2.58	2.70	30	16	1.85
120	16.75	23.45	195	104	13.13	16.75	139	74	1.97	3.38	3 58	30	16	1.87

The average value of the "temperature coefficient" of the rate, or the factor by which the rate is multiplied for a rise of 10° in the temperature, may be found by taking the cube root of the ratio between the rates at 30° and 0° C.; it is 1.85. The coefficients determined from the measurements at 30° and 25° C. (which are entered in the table "at 25°") are practically the same, or if anything, a little higher, see Table XIII.

Appendix

Magnanini's experiments, carried out in 1890,[1] some of those of Ostwald's[2] and the experiments of Noyes[3] are here recalculated.

At the head of each table I have given the initial composition of the reacting mixture, the numbers divided by 100,000 denoting gram-formula weights of the reagent initially present, the volume being 10 cc in all of Magnanini's and Ostwald's measurements, while in Noyes' the numbers recorded are for a volume of 1 litre. In all these experiments the temperature was 25° C. Mr. F. C. Bowman's experiments were carried out in this laboratory at 0° C., and the numbers recorded from his experiments are for a volume of 1 litre.

[1] Gazz. chim. Ital., 20, 377 (1890).
[2] Zeit. phys. Chem., 2, 127 (1888).
[3] Ibid., 18, 118 (1890).

In the first column of the tables (under t) is entered the duration of the experiments in minutes; in the second, the amount of iodine liberated x (in cubic centimeters of $n/100$ thiosulphate); where Magnanini gave the result of duplicate experiments, I have taken the average. In the third and last column I have entered the value of the constant K of the equation:

$$\frac{1}{V}\cdot\frac{dx}{dt} = K(A-x)\,(B-x)\,(C-x)^2V^{-1}$$

where A, B and C are taken from the heads of the table, and V is the volume in litres, *e.g.*, for Table XV, A = 11.11, B = 7.41, C = 24.07, V = 0.01. See page 685.

In computing the values of K, I made use of "The Method of Areas," described by Mr. R. E. De Lury.[1]

In order to facilitate comparison of the values of K so obtained, I have brought them together in the last table. The constants bracketed have been calculated from the experimental data by making use of the temperature coefficient 1.85 obtained from Table XIII. In the experiments where excess of hydrochloric or nitric acid was used, Magnanini's values agree with my own for the same temperature; replacing these monobasic acids by sulphuric acid, takes about 33 percent of K, corresponding to a difference of 12 percent in the dissociation, which is a fair agreement with the results of measurements of the electrical conductivity. In the experiments in which the concentration of the hydrion was large, the constants are uniform; where however their concentration is small, the constant shows a falling off. This is in line with the results of Mr. W. C. Bray's experiments on the oxidation of hydrogen iodide by chloric acid.[2]

The values of the constants derived from Ostwald's measurements are somewhat smaller than those from the corresponding measurements of Magnanini. Addition of chloric acid and of hydrobromic acid increases the constant

[1] Jour. Phys. Chem., 10, 425 1906.
[2] Ibid., 7, 92 (1903).

very slightly, due no doubt to the oxidation of the bromide or to the reduction of the chlorate.

Noyes and Scott worked with the potassium salts of bromic acid and hydriodic acid in presence of a constant amount of hydrochloric acid; their constant agrees very closely with my own.

Magnanini's Measurements

TABLE XIV

$HBrO_3$, 1.85; HI, 11.11

t	x	$K \times 10^{13}$
5	0.82	142
12	1.44	119
13	1.46	116
21	1.84	100
25	2.05	99
41	2.72	93
52	2.96	91
84	3.69	88
91	3.80	89
175	4.82	86

TABLE XV

$HBrO_3$, 1.85; HI, 11.11; HCl, 11.11

t	x	$K \times 10^{13}$
2	0.82	99
3	1.05	87
9	2.35	84
15	3.27	85
17	3.38	81
28	4.38	84
31	4.50	83
35	4.68	84
40	5.10	86

TABLE XVI

$HBrO_3$, 1.85; HI, 11.11; HCl, 22.22

t	x	$K \times 10^{13}$
2	1.43	85
6	2.98	83
12	4.19	80
17	4.93	80
18	5.06	80
20	5.28	81

TABLE XVII

$HBrO_3$, 1.85; HI, 11.11; HCl, 33.33

t	x	$K \times 10^{13}$
2	2.03	83
4	3.17	82
6	3.93	81
8	4.52	81
10	4.90	80
11	5.08	79

TABLE XVIII

$HBrO_3$, 1.85; HI, 11.11; HCl, 44.44

t	x	$K \times 10^{13}$
2	2.55	68
4	3.94	70
6	4.72	70
7	5.15	72
8	5.33	72

TABLE XIX

$HBrO_3$, 1.85; HI, 11.11; HNO_3, 22.22

t	x	$K \times 10^{13}$
2	1.37	82
6	2.88	78
12	4.19	77
17	4.84	77
19	5.14	78

TABLE XX

$HBrO_3$, 1.85; HI, 11.11; HNO_3, 33.33

t	x	$K \times 10^{13}$
2	2.03	77
4	3.06	73
6	3.83	72
8	4.41	72
10	4.89	72
11	5.03	72

TABLE XXI

$HBrO_3$, 1.85; HI, 11.11; HNO_3, 44.44

t	x	$K \times 10^{13}$
2	2.57	68
4	3.80	67
6	4.60	66
8	5.19	67

TABLE XXII

$HBrO_3$, 1.85; HI, 11.11; H_2SO_4, 5.55

t	x	$K \times 10^{13}$
2	0.68	81
9	2.10	71
17	3.07	69
31	4.20	69
46	4.81	67
51	4.94	66
56	5.27	68

TABLE XXIII

$HBrO_3$, 1.85; HI, 11.11; H_2SO_4, 11.11

t	x	$K \times 10^{13}$
2	1.04	57
9	2.99	53
20	4.51	52
25	4.87	52
28	5.11	52
31	5.26	52

TABLE XXIV

$HBrO_3$, 1.85; HI, 11.11; HCl, 22.22

t	x	$K \times 10^{13}$
2	1.83	43
9	4.32	39
12	4.95	39
13	5.09	39
17	5.55	38

TABLE XXV

$HBrO_3$, 5.55; HI, 11.11

t	x	$K \times 10^{13}$
2	1.23	106
6	2.55	96
9	3.25	95
12	3.78	94
15	4.23	93
21	4.88	93
23	5.02	95
24	5.02	91
27	5.34	92

TABLE XXVI

$HBrO_3$, 9.26; HI, 11.11

t	x	$K \times 10^{13}$
2	2.30	91
4	3.56	90
6	4.36	89
8	4.94	88
10	5.43	89

TABLE XXVII

$HBrO_3$, 1.85; $KBrO_3$, 3.70; HI, 11.11

t	x	$K \times 10^{13}$
2	0.83	116
6	1.85	107
9	2.46	107
12	2.75	99
17	3.41	99
20	3.60	96
28	4.25	96
41	4.86	95
46	5.15	96

TABLE XXVIII

$HBrO_3$, 1.85; $KBrO_3$, 9.25; HI, 11.11

t	x	$K \times 10^{13}$
2	1.38	104
6	2.68	88
9	3.36	88
12	3.87	87
18	4.65	87
22	4.97	87
25	5.16	86

Ostwald's Measurements

TABLE XXIX

$HBrO_3$, 1.856; HI, 11.11

t	x	$K \times 10^{13}$
1	0.22	—
21	1.89	93
41	2.81	92
81	3.93	94
146	4.83	94
201	5.37	96
301	5.89	96
431	6.36	98

TABLE XXX

$HBrO_3$, 1.856; HI, 11.11; H_2SO_4, 5.55

t	x	$K \times 10^{13}$
9	2.04	59
17	3.07	61
31	4.17	63
56	5.27	64
71	5.67	64
97	6.14	65
115	6.39	65

TABLE XXXI

$HBrO_3$, 1.85; HI, 11.11; HCl, 11.11

t	x	$K \times 10^{13}$
9	2.46	85
17	3.54	84
31	4.63	84
41	5.20	85
51	5.60	86
61	5.90	87
71	6.20	85

TABLE XXXII

$HBrO_3$, 1.85; HI, 11.11; HNO_3, 11.11

t	x	$K \times 10^{13}$
9	2.44	84
17	3.51	82
31	4.63	82
41	5.18	84
51	5.55	81
61	5.86	80
71	6.09	80

TABLE XXXIII

$HBrO_3$, 1.85; HI, 11.11; $HClO_3$, 11.11

t	x	$K \times 10^{13}$
9	2.54	90
17	3.54	88
25	4.35	89
33	4.77	88
41	5.18	88
51	5.56	88
61	5.85	89

TABLE XXXIV

$HBrO_3$, 1.85; HI, 11.11; $HClO_4$, 11.11

t	x	$K \times 10^{13}$
9	2.43	85
17	3.52	82
25	4.25	84
33	4.71	83
41	5.15	84
51	5.56	85
61	5.78	85

TABLE XXXV

$HBrO_3$, 1.85; HI, 11.11; H_2SO_3, 5.55

t	x	$K \times 10^{13}$
9	2.40	81
17	3.41	80
25	4.16	81
33	4.65	81
41	5.05	81
51	5.40	81
61	5.76	81

TABLE XXXVI

$HBrO_3$, 1.85; HI, 11.11; HBr, 11.11

t	x	$K \times 10^{13}$
9	2.59	89
17	3.68	90
25	4.43	92
33	4.94	93
41	5.34	94
51	5.72	95
61	6.04	96

Noyes' Measurements

TABLE XXXVII

$KBrO_3$, 166; KI, 1000; HCl, 4000

t	x	$K \times 10^{13}$
2	112	63
4	192	62
7	279	62
11	358	62
16	423	62
22	479	62
30	526	62
40	562	62

TABLE XXXVIII

$KBrO_3$, 83; KI, 500; HCl, 4000

t	x	$K \times 10^{13}$
1.5	46	65
3	88	68
5	125	66
8	180	70
12	233	70
17	261	72
23	294	73

TABLE XXXIX

$KBrO_3$, 83; KI, 1000; HCl, 4000

t	x	$K \times 10^{13}$
1.5	48	68
3	90	68
5	134	68
8	179	65
12	223	63
17	258	60
23	290	60

TABLE XL

$KBrO_3$, 83; KI, 500; HCl, 4000

t	x	$K \times 10^{13}$
2.5	40	68
5.5	79	68
9	112	72
15	155	71
23	194	72
36	235	74
58	275	71

F. C. Bowman's Measurements

TABLE XLI

$KBrO_3$, 55.26; KI, 4960; H_2SO_4, 1666.6

t	x	Percent bromate decomposed	$K \times 10^{11}$
6	62.4	18.8	98
19	155.8	46.8	98
30	206.6	62.3	99
40	238.8	72.1	99
50	261	78.7	98
60	276.4	83.3	97
70	290.2	87.6	97
80	299.6	90.2	97
100	315.6	95.1	98

TABLE XLII
SUMMARY OF TABLES

Experimenter	Table	Initial Composition (Vol. = one litre)	K × 10^{13} for 30° C	K × 10^{13} 25° C	K × 10^{13} 0° C
Clark:	XIII	$KBrO_3$, 82; KI, 394.7; HCl, 760	100	73	16
Magnanini:	XIV	$HBrO_3$, 185; HI, 1111	(139)	102	(22)
	XV	" " + HCl, 1111	(117)	86	(19)
	XVI	" " + HCl, 2222	(112)	82	(18)
	XVII	" " + HCl, 3333	(111)	81	(18)
	XVIII	" " + HCl, 4444	(96)	70	(15)
	XIX	" " + HNO_3, 2222	(107)	78	(17)
	XX	" " + HNO_3, 3333	(100)	73	(16)
	XXI	" " + HNO_3, 4444	(92)	67	(15)
	XXII	" " + H_2SO_4, 555	(96)	70	(15)
	XXIII	" " + H_2SO_4, 1111	(73)	53	(12)
	XXIV	" " + H_2SO_4, 2222	(55)	40	(9)
	XXV	$HBrO_3$, 555; " — —	(130)	95	(21)
	XXVI	$HBrO_3$, 1111; " — —	(122)	89	(19)
	XXVII	$HBrO_3$, 185; HI, 1111 + $KBrO_3$, 370	(137)	100	(22)
	XXVIII	" " + $KBrO_3$, 925	(123)	90	(20)
Ostwald:	XXIX	$HBrO_3$, 185; HI, 1111	(130)	95	(21)
	XXX	" " + H_2SO_4, 555	(86)	63	(14)
	XXXI	" " + HCl, 1111	(116)	85	(19)
	XXXII	" " + HNO_3, 1111	(112)	82	(18)
	XXXIII	" " + $HClO_3$, 1111	(120)	88	(19)
	XXXIV	" " + $HClO_4$, 1111	(115)	84	(18)
	XXXV	" " + H_2SO_3, 555	(111)	81	(18)
	XXXVI	" " + HBr, 1111	(127)	93	(20)
Noyes and Scott:	XXXVII	$KBrO_3$, 166; KI, 1000; HCl, 4000	(85)	62	(14)
	XXXVIII	" KI, 500; HCl, 4000	(94)	69	(15)
	XXXIX	$KBrO_3$, 83; KI, 1000; HCl, 4000	(89)	65	(15)
	XL	" KI, 500; HCl, 4000	(97)	71	(16)
Bowman:	XLI	$KBrO_3$, 55.26; KI, 4960; H_2SO_4, 1666	(71)	(45)	10

Summary

(1) The rate at which iodine is liberated in solutions containing potassium bromate, potassium iodide and hydrochloric acid is proportional to the concentration of the bromate, the concentration of the iodide, and the square of the concentration of the acid.

(2) In solutions containing potassium bromate, iodide, bromide and hydrochloric acid the two haloid salts are oxidized independently.

(3) The potassium triiodide formed by the oxidation of iodide adds very slightly to the rate of reduction of bromate; so that, in first approximation, the effect on the rate produced by the iodine liberated during the reaction may be neglected.

(4) Thus the progress of the reaction may be expressed by a simple differential equation (see equation 1, p. 685), which is shown to be in accordance with the experiments. A term to represent the effect due to the bromide formed during the reaction may be introduced into the equation (see equation 3).

(5) Raising the temperature 10° multiplies the rate by 1.85.

(6) The equations developed in this paper have been used to recalculate Magnanini's, Ostwald's and Noyes' measurements. (See Appendix.)

These measurements were carried out in the chemical laboratory of the University of Toronto during the winter of 1904–5; and in conclusion, I wish to express my sincerest thanks to Prof. W. Lash Miller for suggesting this research and for his supervision throughout the work.

The University of Toronto,
June, 1906

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ALLOTROPIC SILVER AND ITS COLORS

BY F. E. GALLAGHER

A discussion of the cause of the colors of colloidal metals is given in a paper by Stoeckl and Vanino.[1] Several possible explanations, which depended on the behavior of light rather than on a distinctive property of an allotropic form, were offered. The work of Christiansen[2] on colors depending on the refractive indices of a transparent solid and a containing liquid, was revised and applied to the case of colloidal suspensions. In another division the possible relations of light absorption to the colors of colloidal suspensions were developed. Under this explanation the colors are supposed to be dependent on the thicknesses of the colloidal particles or films—the various thicknesses letting through light of greater or lesser wave-length. Some experiments of this kind seemed to be a step in the right direction, for it hardly seemed reasonable that the different colors were due to the existence of several allotropic forms of a metal as some previous experimenters were led to believe. Stoeckl and Vanino performed no direct experimental work to prove or disprove any of their various suggestions, so this work was undertaken with the hope of finding that the colors of colloidal silver were due to some physical phenomenon, and to discuss which one best explained the facts.

Previous Work

The first work of importance on colloidal silver was done by Carey Lea,[3] who studied the methods of preparation, and obtained allotropic silver of many colors. This work was later extended by Blake,[4] who made a simpler classification

[1] Stoeckl and Vanino: Zeit. phys. Chem., 30, 194 (1899).

[2] Christiansen: Wied. Ann., 23, 298 (1884).

[3] M. Carey Lea: Phil. Mag., 31, 320, 238, 497; 32, 337.

[4] Blake: Am. Jour. Sci., 16, 282 (1903). Cf. Gutbier and Hofmeier: Zeit. anorg. Chem., 45, 77 (1905).

of the facts that silver existed in three or possibly four allotropic forms: white, blue and red, with yellow as the possible fourth. The other colors, to which Lea had assigned separate forms, were supposed to be mixtures of these three or four classes. Blake also tried to find definite conditions for the formation of the different forms, but found that at best they were somewhat uncertain. The conclusions of Lea and Blake will be discussed further on in this paper.

The Christiansen Effect

Christiansen[1] has shown that color can be a refractive index phenomenon when a transparent solid is in a liquid medium. Ordinary glass has a refractive index of about 1.54, carbon tetrachloride of 1.46, benzene 1.51, and carbon bisulphide 1.64. Since the three liquids are miscible in all proportions, it is thus possible to have a liquid with a refractive index anywhere between 1.46 and 1.64. We can thus get a containing medium of the same refractive index as the glass for any one wave-length, since the above figures vary for the different spectrum lines. If we put a piece of glass into benzene and add carbon bisulphide, the glass practically disappears as the refractive index of the solution approaches that of the glass. At the same time the solution becomes colored. If the glass powder be finely ground, the color effects are brighter. There is of course no refraction of the particular wave-length for which the glass and the solution have the same index of refraction. If this were the only wave-length transmitted, we should have a convenient method of obtaining monochromatic light of any desired wave-length. Although this method was recommended by Christiansen, it does not seem a practical one for obtaining monochromatic light. If the layer of glass be thick, very little light is transmitted. If the layer be only moderately thick, so many of the other wave-lengths are transmitted by reflection from the glass surfaces that the effective color is due to them and not to the unrefracted ray. Thus the addition of carbon bisulphide

[1] Wied. Ann., 23, 298 (1894).

with a high refractive index always displaced the apparent color toward the red end of the spectrum in spite of the fact that the refractive index of the glass is higher for blue light than for red light. The phenomenon is really one of relative dispersions.

Although the transmitted light seemed to the eye to be rather pure, a spectroscopic examination showed that it corresponded to quite a broad band, containing relatively large amounts of the neighboring colors. As carbon bisulphide was added the apparent color changed toward the red, which change was accompanied by a shifting of the spectrum band in that direction. More and more of these other colors can be cut out by increasing the thickness of the layer, but this cuts down the amount of transmitted light so much that by the time the layer is thick enough to restrict the color to blue for instance, very little blue is transmitted.

When repeating Christiansen's experiments it was found unsatisfactory to examine the color against the sky as he suggests, because the color is dependent upon the position in which one holds the vessel in reference to the light and eye, and because the source of light is of variable intensity and not strong enough. By protecting the eyes so that only the transmitted light falls upon them, sunlight can be used; but very satisfactory and uniform results were obtained by using a lantern projection dish (1 cm × 5 cm × 7 cm) in an arc lantern which threw the color on a white screen.

The experiments were first tried with pulverized glass. Instead of grinding in water and drying preparatory to using with benzene, etc., the glass was ground in benzene from which the fine portions were floated out and used. The finest ground glass gave the purest colors. A projection dish was about half filled with the glass and 20 cc of benzene added. The transmitted light was blue. When carbon tetrachloride was added 0.5 cc at a time the blue became deeper, then violet and at last almost black, very little light being transmitted when the refractive indices of the glass and liquid were greatly different. Now upon the addition of

CS_2 the color was again carried through the blue, green, poor yellow to a brown-red, and, on further addition, again to a black. This can be reversed indefinitely. The dish is shaken on the addition of each portion to make the liquid homogeneous.

This worked equally well with salt, an isotropic crystal form, though it was here necessary to work with a thinner layer, obtained by placing a piece of plate glass in the dish.

Interesting results can be obtained with biaxial transparent crystals,[1] which are complicated by two refractive indices, and with colored salts. This was, however, tried only in the case of copper sulphate in benzene, the blue color of which was replaced by a green on addition of carbon bisulphide, but which could not be carried to a red.

Christiansen Effect Applied to Colloidal Silver

Experiments were made to investigate the relation of refractive index to colloidal silver solutions. The general scheme was to see if changing the refractive index of the liquid by means of other solvents gave color changes in accord with the theory. The silver was reduced to the colloidal state by Carey Lea's method from a silver nitrate solution by means of Rochelle salts and ferrous sulphate. The silver nitrate, Rochelle salts and ferrous sulphate solutions contained 1 gram of salt per liter. Solutions of different concentrations were prepared from these. The following table gives a typical set of solutions.

SET A

Solution number		1	2	3	4	5	6
I	$AgNO_3$	2 cc	2 cc	2 cc	2 cc	2 cc	2 cc
	Rochelle salt	1 "	1 "	1 "	1 "	1 "	1 "
	Water	0 "	2 "	4 "	8 "	16 "	32 "
II	Water	0 cc	2 cc	4 cc	8 cc	16 cc	32 cc
	$FeSO_4$	½ "	½ "	½ "	½ "	½ "	½ "
	Rochelle salt	1 "	1 "	1 "	1 "	1 "	1 "

[1] Christiansen: Wied. Ann., 23, 301 (1884).

II was poured into I. This gave solutions with a $AgNO_3$ concentration varying from 0.5 gram to 0.03 gram per liter. The solutions were prepared in test-tubes, placed near a window having a northern exposure, and allowed to develop.

It was found that such a set of solutions would give a wide variety of colors. Solution No. 1, the most concentrated, would reduce quickly and would color a yellowish brown. Within a few minutes No. 2 came down blue, but in the course of a half hour had changed through a green to a yellow or yellow-brown. The more dilute solutions first came down blue. At the end of several hours the colors were as follows: 1 and 2, yellow-brown; 3, green; 4, 5, 6, blues of falling intensity. This is not an exact program of what will happen every time, for it was found that uncontrollable and even unknown conditions influence the formation of the colloidal solution. On repetition it often happened that No. 2 would become yellow at once, without first becoming blue. The general law, however, holds that the color tends to approach the red end of the spectrum with increasing concentration, and that the change with time is always in that direction. In no case of simple reduction in water solution did a color change toward the violet end of the spectrum. After considerable time even the dilute solutions of set A became yellow, and from the yellow or yellow-brown solutions the silver separated as a black powder.

Similar sets of solutions were prepared, which separately contained NH_4OH, a large excess of reducing agent, and KNO_3 for an electrolyte. There were no striking differences shown. In the ammonia solution the colors formed more slowly; the electrolyte had but little effect, and the reducing agent the more quickly threw out the silver as a black powder.

The conclusion drawn from the behavior shown by Set A of solutions was that the color of the colloidal silver solutions was due in some way to the coagulation or concentration of the colloid, the finer particles or the presence of small amounts of those particles giving colors toward the violet end. As the coagulation or concentration increases, the

color approaches the red end. A further explanation of this will be given later. The production of so many colors in this way seemed to indicate that the color could hardly be due to different allotropic forms. The attempt to change these colors by various solvents was next tried. There is no convenient liquid having a refractive index lower than water, for which $\mu = 1.331$ at 20°. We used necessarily liquids with higher refractive indices, such as acetone, $\mu = 1.36$; ethyl alcohol, $\mu = 1.36$; and benzene, $\mu = 1.5$. Benzene was used in alcoholic solution so as to render it miscible with water. The addition of these liquids had a marked effect on the color. Acetone was added to a bluish green solution, which in a few moments became deeper blue. When acetone was added to a yellow-brown solution, the latter changed to a green. In these cases 2 cc of acetone were added to 2 cc of solution. Alcohol behaved in much the same way. When benzene was added to the alcoholic solution it seemed to carry the color even further toward the violet.

Since we were supposing that this change of color was due to the change of refractive index, we ought to reverse the color change by again decreasing the refractive index. To solutions which had been turned violet by the addition of alcoholic benzene, and which had a refractive index greater than 1.36, large excesses of water and of alcohol were added. The excess of water caused the benzene to separate as a second liquid layer; the alcohol was simply a diluting agent. In neither case was there a marked color change, nothing that could be called a reversal. Other trials gave similar results. This point was against the refractive index idea.

The effect of varying amounts of the alcohol, acetone, etc., on the colors of the solutions was next tried. To 2 cc of a yellow-brown solution, alcohol was added in amounts varying from 1 drop to 2 cc. At the end of one-half hour the colors varied from a yellow to a green, in order of amounts of alcohol used. The color effect with different solvents is not due then to traces of the substances, but depends upon the amount.

Solutions treated with alcohol, acetone, benzene, etc., do not change (toward the red end) on standing in the light, as was shown to be the case in Set A, which were simply in water solution. If a solution went blue on adding alcohol, it stayed blue until the black silver powder precipitated. We come to the conclusion therefore that the different solvents act in some way as decoagulators, displacing the color toward the violet end and preventing the change which in their absence causes the metallic silver to precipitate from yellow or red solutions.[1]

Light is essential to the various color changes. A series like Set A if made up in the dark and left there will remain colorless, except for a slight yellow coloration in the most concentrated solutions. If exposed to diffused daylight the color formation takes place slowly. If exposed to direct sunlight the change takes place very quickly. Light is necessary in producing the color changes caused by alcohol, acetone, etc. Four cc of alcohol were added to 2 cc of a yellow solution in the dark. No change occurred as long as it was in the dark, but when placed in the focus of an arc lamp, the solution quickly went greenish blue. A whole series of solutions containing alcohol, acetone and benzene were made up and left in the dark for a week; aside from some yellow colorations no change occurred. Upon being exposed to sunlight various colors quickly appeared. Many experiments on the effect of light were made, all of which showed that but very slight color changes occur without it.

These facts would seem to dispose definitely of the possibility of the color being due to the Christiansen effect, for if the color were a phenomenon that depended upon a change of refractive index, then upon the addition of such a liquid as alcoholic benzene to the containing medium, the refractive index of that medium at least would have to change, even in the dark, thus giving some difference in color. Since no

[1] It is possible that something of this sort was the cause of Faraday's apparently contradictory results with colloidal gold. Phil. Trans., 147, 165 (1857).

change occurs in the dark, the refractive index cannot be responsible for the colors of colloidal silver.

This brings us to what seems to be the most plausible idea, that the colors are due to a light absorption effect depending upon the thickness of layer, degree of coagulation, or concentration of colloidal silver particles in the solution, any of which would have about the same effect, by cutting down the total light transmitted. Gold and silver have been shown to be translucent in thin films, and to possess both strong reflective and strong selective absorption. By selective absorption is meant that some particular wave-lengths are more strongly absorbed than others, and so the light transmitted is stronger for some wave-lengths.

Quite a number of facts indicate that this is the case. Other investigators have reported that the color of silver films depended on the thickness. Foucault[1] says that in thin layers metallic silver is blue. Bothe[2] reports the same. Christomanos[3] found very thin layers of silver to be blue, thicker layers blue-green and still thicker ones yellow or yellow-brown. The purest colors obtained by us were at the blue end. The yellows were brown-yellows, and the reds, brown-reds. Brown is a mixture of red, yellow and blue, so its presence is well explained in this way. An examination of the light transmitted through different colored colloidal mirrors, always showed, when examined by a spectroscope, the presence of considerable quantities of blue. The blue mirrors also contained colors corresponding to longer wave-lengths, but not in quantities to compare with the blue light transmitted, while in the yellow and red mirrors the blue seemed to be quite an important constituent. This could not occur if the mirrors were optically homogeneous. A spectro-photometric study of the mirrors is much to be desired.

If the colors of colloidal silver are to be explained by this theory[4] it is necessary to show that increasing the depth even

[1] Foucault: Comptes rendus, 63, 413 (1866).
[2] Bothe: Jour. prakt. Chem., 92, 191 (1864).
[3] Christomanos: Zeit. Chemie, 1869, 310.
[4] Cf. Siedentopf and Zsigmondy: Drude's Ann., 10, 1 (1903).

of a colloidal silver solution would cause the color to shift toward the red. Solutions of different colors corresponding to Set A, already described, were made up in 200 cc portions. In order to study the effect of varying the depth of layer a tube 2 cm in diameter and 50 cm long was ground off at one end, to which a piece of plate glass was cemented. The walls of the tube were then covered with black paper, to exclude light from the sides. The sunlight was reflected by means of a mirror directly up through the tube, thus providing a strong illumination and making it possible to obtain light through quite a depth of liquid. Without a strong light the liquid soon absorbs so much light that but very little variation of the thickness of the liquid is possible. By means of this arrangement it was shown that varying the thickness of a liquid layer of colloidal silver did shift the color toward the red end in a most remarkable way. A small amount of a green solution was placed in the tube. As more solution was poured in, the strength of light was greatly decreased and the solution took on a distinctly yellower color. Upon being removed from the tube the solution was still the original green color. The change to a yellow was therefore not due to the sunlight having coagulated the green solution. It was to prevent this that alcoholic solutions were used, for as has already been shown they are not changed toward the red end of the spectrum by sunlight. A brown-yellow solution which was studied in the same manner, appeared as a beautiful red. The most successful of these experiments was made on a greenish blue solution, which went brownish yellow and finally a brown-red on increasing the depth of the absorbing layer.

After this surprising agreement with the theory it remained to show that the colloidal mirrors behaved in the same way. To do this it was necessary to prepare blue colloidal mirrors, for if we had the thinnest mirrors which would be the blues, we hoped to make the others by using several thicknesses of the blue ones. Good blue mirrors were very easily made by Carey Lea's[1] recipe for making "gold- and copper-

[1] Carey Lea: Phil. Mag. [5], 31, 320 (1891).

colored colloidal silver," in which he uses 40 grams of NaOH and 40 grams of dextrine dissolved together in two liters of distilled water; 28 grams of $AgNO_3$ in solution are very slowly added and stirred in. In this way a reddish-brown, almost black solution of colloidal silver was obtained. Into this solution chemically clean glass plates were dipped, after which they were put in an oven and dried at 50°–60° C. Since the silver was in solution as colloidal silver, it was deposited as a colloidal film, blue by transmitted light, upon removing the solvent. The fact that blue colloidal silver is deposited from a reddish brown solution in this way would in itself seem to argue against red and blue colloidal silver as different allotropic forms.

An attempt was made to show that several blue mirrors placed together would give a green, yellow or red transmitted color. This did not succeed because too little light was transmitted, owing to the increased absorption in the several pieces of glass, and to the fact that a film on each piece of glass, which was coated on both sides, was presenting a fairly good reflecting surface. The mirrors were next deposited successively one on another from the same solution. As many thicknesses as desired could therefore be obtained on one piece of glass. Each coating was dried before the next was added, and the successive deposits were not carried quite to the height of the preceding one, thus giving on the finished plate a series of bands consisting of one, two, three, etc., thicknesses of the colloidal mirror. On one plate the effect of different thicknesses could be seen, and it did show that here as in the case of liquids the thickness of the layer determined the color. A specimen of a plate obtained is given in Fig. 1.

The different successive deposits are given by the numbers 1, 2, 3, etc. The first two were blue, the third showed a fairly good green, the lower ones showed red in increasing amounts, not even the fourth exhibiting a satisfactory yellow, although yellows were obtained on some other plates. The strips marked "*a*," "*b*," "*c*," etc., were due to the fact that after dipping the dry plate into the solution the surface tension

1	Blue
a	Yellow
2	Blue
b	Yellow
3	Green
c	
4	Yellow and Red
d	
5	Yellow-Brown and Red
e	
6	Red
f	
7	Red

Fig. 1

between the dry undipped portion and the liquid held a band of solution thicker than that just below it which drained better. So here on the edge of each new film we had a deposit from a deeper layer of liquid, which necessarily made a thicker mirror at that place, and in turn gave an absorption effect equivalent to several successively deposited thin films. Thus we had at "*a*" a fairly good yellow between two blues. This in itself was fortunate for it was possible that the character of the deposit might vary, depending on whether it were deposited on glass or on silver. In other words the silver might cause the formation of a different allotropic form (further coagulation or some other effect that would change the color of the second film). The fact that the second film remained blue even when deposited on silver and that an intermediate film of yellow was obtained rather disproved this possibility.

As a further proof that the different colors obtained were really "blue" silver in different thicknesses and not due to further coagulation, allotropic forms or some other reason,

it remained to show that decreasing the thickness of the yellow, green, and red mirrors caused the transmitted color to again become blue. It was possible to do this because colloidal silver is soluble in water. The plate was allowed to stand edgewise in a large quantity of water, so that there was dissolved only the right-hand half of the deposits. the left-hand half remaining in its original form for comparison. When the plate was removed from the water and dried, a beautiful blue was found to have replaced the former yellow, green, and red. When the plate was wet the yellow solution of dissolving silver obscured the real color of the plate. (It will be remembered that the mirrors were first deposited from a deep brown solution, which on dilution became yellow. The dissolving silver gave a similar solution.) If the yellow or red forms had been caused by coagulation of the blue form, we should expect them to be less soluble than the blue, which was in a finer state of division and consequently we should have expected the blue to have dissolved first, leaving the other colors, provided always that the mirrors are pervious to water.

For the guidance of any one who should at any time repeat these experiments it would be well to explain that the color effects obtained in the experiments on varying the thickness of the colloidal layer, both in the liquids and mirrors, were not always distinct or brilliant. Some very conclusive results were obtained when working with liquid layers, but because of the great light absorption when working with increasing depth of liquid it is not possible to pass from a deep blue to a brilliant red by the use of one solution. Likewise, the colors obtained on the mirrors were sometimes dull, yet on the whole, conclusive, and this also is to be expected for throughout the work it has been found that the variables influencing the production of the different colors are many and hard to control, and would assert themselves as much in methods dealing with the successive production of the colors, as under simpler conditions.

Summary

In this investigation it has been shown that:

(1) Colloidal silver solutions of all colors can be easily prepared, from one set of reagents, by varying simple conditions. Since the color changes can be brought about also by varying the thickness of the solution, the colors cannot be due to allotropic modifications.

(2) Certain organic solvents have been found to act as "decoagulators," preventing the light from producing the color changes in the colloidal suspension, which occur in solutions not so treated. Their action depends on the amount used. These solvents do not prevent the precipitation of metallic silver but do affect the color of the solution from which the silver separates.

(3) The color changes in colloidal silver solutions are not satisfactorily explained by the Christiansen refractive index phenomenon. A color change produced by increasing the refractive index of the liquid was not reversed when the refractive index was again diminished. No change of color occurred when the refractive index was changed in the dark, which showed that the color changes depended on a direct action of light upon the colloidal suspension and not on a change of refractive index.

(4) Light is essential to the changes of color, and the speed of these changes depends on the intensity of light. The light is supposed to cause the coagulation of the colloidal suspension, thus increasing the size of the particles, or to affect the concentration of the particles in solution by increasing the reduction of the silver nitrate to colloidal silver.

(5) The color of colloidal silver is due to a selective light absorption. With increasing thickness of the absorbing layer or with increasing size of the particles the amount of blue light transmitted decreases relatively much more rapidly than does the amount of red light transmitted. This points to internal selective reflection.

Conclusion

There is only one form of colloidal silver, not several allotropic colloidal forms, and the various colors and properties such as electrical conductivity, density, action toward reagents, etc., concerning which much has been written, are to be explained by the state of aggregation or number of the particles of this colloidal form.

This investigation was suggested by Professor Bancroft and has been carried on under his supervision.

Cornell University.

COPPER CATHODES IN NITRIC ACID

BY J. W. TURRENTINE

It is known that nitric acid in dilute solutions undergoes reduction, quantitatively, at the cathode. This method is recommended for the quantitative determination of nitrates. This reduction is equivalent, of course, to an action by nascent hydrogen, liberated at the cathode, on the nitric acid, according to the equation:

$$8H_2 + 2HNO_3 = 2NH_3 + 6H_2O.$$

Nitric acid in acting on copper, on the other hand, is reduced not to NH_3 but to nitric oxide, as indicated by a free evolution of brown fumes. In other words, copper reduces HNO_3 to NO and not to NH_3. It reduces nitrobenzene to aniline. Why does it not reduce HNO_3 completely? Why does the reduction stop at nitrites?

It was the object of this bit of work to answer these questions.

Since the evolution of NO might be due to the too rapid reaction between the Cu and HNO_3, dilute solutions of the latter, 10 percent, 5 percent and 2½ percent concentrated HNO_3 solutions (10 cc conc. HNO_3, to 90 cc H_2O, etc.), were used consecutively and pulverulent copper added. In each case nitric oxide was evolved, showing that reduction, if any, was not complete. Tests were also made in each case for NH_3, but nothing more than traces were detected (coloration of litmus). That the reaction might be still slower a clean copper strip was placed in the 10 percent HNO_3 solution and left there for two days; no ammonia was produced, though there were no visible red fumes. These experiments were then varied by (1) the addition of KNO_2 for nitrites, (2) by the addition of KNO_3 and bubbling of H_2 through the solution, and (3) by stirring. The results were negative. Again they were varied by the addition of H_2SO_4 to the solutions containing the pulverulent Cu and the copper strip and stirring, still with no results.

Attention was then turned to the electrochemical side of the subject. Accordingly, a 5 percent solution of HNO_3 was electrolyzed between copper electrodes at a current density of 8 amp/dm^2. Gas was evolved freely at the cathode. Judging by the smell, it was nitric oxide. Also, NH_3 was formed in detectable amounts.

It was noticed in connection with this experiment that gas was evolved freely at the cathode and that the gas was probably NO; that no gas was evolved at the cathode when a platinum anode was used from the beginning; that even with a copper anode no gas was evolved at the cathode until the solution of $Cu(NO_3)_2$, collecting in the bottom of the vessel due to its greater specific gravity, reached the bottom of the cathode. Then, at that point, gas was evolved. This evolution of gas continued after the electrolysis was stopped. These phenomena were noticed repeatedly. To determine the composition of the gas given off at the cathode the following experiment was made:

In a gas coulometer were placed two copper strips as electrodes, connected in circuit by wires thrust through the stopper which closed the coulometer. The lower parts of the electrodes were coated with paraffine to prevent short-circuiting. The coulometer was then filled with 10 percent HNO_3 solution and a current was passed that gave a density of about 8 amp/dm.^{2} As soon as the concentration of the $Cu(NO_3)_2$ became considerable gas began to be evolved. Portions were withdrawn from time to time for analysis and showed the following composition:

NO = 80 percent; H_2 = 3 percent; nitrogen (by diff.) = 17 percent.

NO was determined by absorbing the gas in 10 percent $FeSO_4$ solution; H_2, by palladium absorption. The residue was taken as nitrogen. There may have been some other oxides of nitrogen.

It became evident from the foregoing experiments that HNO_3 could not be reduced quantitatively to NH_3 in the presence of Cu ions, and that the reduction stops at the nitrite

stage. This was further established by an experiment in which a solution of HNO_3, composed of 100 cc concentrated HNO_3 to 200 cc H_2O, was electrolyzed between double platinum anodes and a small (2×5 cm) copper cathode. A current (7 amp.) was passed of such cathode density that no copper was dissolved. Under these conditions no gas was evolved at the cathode and the reduction to NH_3 was large. When the current density, however, was allowed to drop off so that some copper was dissolved, NO was given off abundantly at the cathode and a greatly increased current density was necessary to effect complete reduction again.

Upon such evidence, then, it was decided that the presence of Cu ions in solution prevented the reduction of HNO_3 to NH_3 and caused the production of nitrites when copper was dissolved in HNO_3.

Accordingly, efforts were made to find some anion which would form an insoluble compound with copper cations as fast as the latter were thrown into solution, yet which would not inhibit the solution. If the Cu ions were precipitated as fast as formed, there should be a reduction to ammonia. To effect the chemical precipitation of Cu ions the following substances were used, all giving, however, salts soluble in HNO_3 solutions:

Boric acid, phosphoric acid, sodium phosphate, benzoic acid and potassium sulphocyanate. (The latter reduces HNO_3 to NH_3.)

An attempt, which was successful, was then made to precipitate the Cu ions electrolytically as fast as they were thrown into solution by the chemical reaction between the acid and copper. The apparatus and operation were as follows: Ten percent HNO_3, platinum anode, enclosed in parchment to prevent the oxygen there liberated from diffusing through the solution and causing convection currents; a copper or platinum cathode enclosed in a porous porcelain cup, containing as cathode liquid a solution of NaOH. The electrodes were placed as near as possible to the bottom of the cell. A copper strip was suspended in the HNO_3 solution

and protected from polarization by two paraffine shields (filter-papers covered with paraffine). The strip being suspended in the upper part of the solution and the electrodes in the bottom of the cell, there was less tendency for the current to pass through and polarize the copper. Any such tendency, however, would have been obviated by the paraffine shields. The copper nitrate formed by the chemical action flowed to the bottom of the vessel under the influence of gravity. A current of 1.5 amp. was passed through the solution and carried the copper ions into the cathode chamber where they were precipitated by the NaOH, forming a coating of $Cu(OH)_2$ on the inside of the cup. The NH_4 ions were also carried into the cup where they were tested for by warming a portion of the solution and smelling. Good qualitative tests were obtained. Thus the concentration of copper ions was kept down and the copper then dissolved with but a slight evolution of gas.

That no nitrites were produced at the anode was proved by electrolyzing a 10 percent solution of HNO_3, free from nitrites, with copper anode and platinum cathode, the latter enclosed in a porcelain cup containing NaOH solution, as above. After a run of one-half hour the solution was tested for nitrites with KI, the copper first being removed by NaOH; no nitrates were indicated. A current of 1.5 amp. was used. Anode surface 5×10 cm.

An experiment was performed to determine the amount of gas evolved on dissolving a known amount of copper in nitric acid where no attempt was made to reduce the nitrites produced or to precipitate the ions formed, and to compare this weight and volume with those of copper dissolved under the conditions as obtained in the first experiment above described where the Cu ions are precipitated electrolytically. Accordingly, a copper strip No. 1 of known weight was dissolved, partially, in 10 percent HNO_3 and the evolved gas measured in a gas burette. A like strip No. 2 of known weight was placed in a portion of the same solution but under conditions mentioned above, and the evolved gas caught and measured in an inverted coulometer.

	Amount Cu dissolved	Gas evolved	Time
1	1.25 gms.	100 cc ±	2 hours
2	0.30 "	2.0 cc—	3 "

If No. 2 had evolved gas at the same rate as No. 1, the volume should have been 25 cc instead of 2.0 cc; or, it may be said, 23 cc of NO were reduced to NH_3 by the hydrogen evolved by 0.3 gram Cu dissolving. 0.3 : 1.2 : : X : 100; X = 25.

This, then, establishes the fact that copper on dissolving in HNO_3 in the absence of copper ions does reduce nitric acid to HN_3.

The question was then suggested—what accelerates the rate of solution of the copper in No. 1 over that of No. 2? Is it the presence of HNO_2 or of Cu ions?

To answer this an additional experiment was made. A copper strip of known weight was suspended in 10 percent solution of HNO_3 composed of 10 cc conc. HNO_3 and 90 cc $2MCu(NO_3)_2$, to which about 2 grams of urea had been added to decompose any nitrites formed. No gas was evolved, unless stirred, though small bubbles collected on the strip. This was No. 3. A second strip, No. 4, was suspended in a solution of same strength as above containing nitrites ($NaNO_2$). These two compared with No. 1 show the following:

	Copper dissolved	Gas evolved	Time
1	?	6.0 cc	1 hour
2	—0.0176 (gain)	None	1 "
3	0.4 gram	90.0 cc	1 "

These results would show that the acceleration is due to the presence of nitrites.

The results of this paper may be summed up:

1. When copper dissolves in nitric acid the anode reaction is the formation of copper nitrate and not of nitrite.

2. When copper dissolves in nitric acid, the cathode reaction is the reduction of the nitric acid. The chief reaction

product is NO when there is copper as ion in the solution, and NH_3 when there is practically no copper as ion in solution.

3. When a solution of copper nitrate and nitric acid is electrolyzed, with a copper cathode, nitric oxide is formed at the cathode.

4. When a solution of nitric acid is electrolyzed, with a copper cathode, ammonia is formed at the cathode.

5. The apparent discrepancy between the chemical and electrochemical action of copper on nitric acid is due entirely to a difference in the conditions under which the two sets of reactions have been performed.

This work was suggested by Professor Bancroft and has been carried on under his supervision.

Cornell University.

PHOTOCHEMISTRY AND THE PHASE RULE.

BY WILDER D. BANCROFT

Draper[1] was the first to point out that only those rays, which are absorbed by a substance, can produce a chemical change in that substance. It does not follow from this that chemical change is produced by all rays which are absorbed. There appears to be a conversion factor for the change of radiant energy into chemical energy and we know practically nothing about the conditions determining the value of this conversion factor. For cases of reversible equilibrium we can predict the direction of the change. Under the influence of light of a given wave-length, we shall have formed the system having the lower conversion factor for the light in question. A special case is the one in which the new compound or compounds do not absorb the particular wave-lengths which are acting on the system. This conclusion has already been formulated in other terms a number of times[2] and its truth is self-evident. We are dealing with an application of the theorem of Le Chatelier. An interesting experimental confirmation of this has recently been given by Regener.[3] Ozone has a maximum absorption in the ultra-violet at 257$\mu\mu$ and light of 200–300$\mu\mu$ converts ozone rapidly into oxygen. On the other hand, oxygen[4] absorbs waves of less than 193$\mu\mu$ and Regener[5] finds that the conversion of oxygen into ozone is caused very largely by light of a wave-length less than 200$\mu\mu$. The color changes of the so-called silver photochloride[6] are in line with this, though the absence

[1] Phil. Mag. [3], 19, 195 (1841).

[2] Elder: Chem. News., 65, 513 (1892); Wiener: Wied. Ann., 55, 257 (1895); Luther: Zeit. phys. Chem., 30, 628 (1899); Wildermann: Ibid., 42, 257 (1902); Bauer: Ibid., 45, 625 (1903). Wildermann's formulation is the exact opposite of what the text shows that he intends.

[3] Drude's Ann., 20, 1033 (1906); Cf. Russ: Elektrochemie, 12, 409 (1906).

[4] Kreusler: Drude's Ann., 6, 419 (1901).

[5] Regener: Ibid., 20, 1040 (1906).

[6] Wiener: Wied. Ann., 55, 225 (1895); Bauer: Zeit. phys. Chem., 45, 613 (1903).

of change in the dark is a point which calls for further investigation.

The change of dissolved sulphur into so-called insoluble sulphur is caused by violet and ultra-violet light, and these solutions absorb the light beyond G. In this particular case, the reverse reaction is not known to be affected by light and the same has been shown by Luther and Weigert[1] to be true for the change of dianthracene into anthracene.

While the difference in the unknown conversion factors for the reacting substances and the reacting products determines the direction of the reaction, there is another factor which is very important in determining the magnitude of the displacement of the equilibrium. Luther[2] has pointed out that a reversible equilibrium under the influence of light is a case of dynamic equilibrium. The displacement of the equilibrium depends on the rate of the reverse reaction. If this is high, the effect due to light is small.[3] If it is low, the effect due to light may be large. Adding anything that will increase the reverse rate will decrease the displacement of equilibrium caused by light of a given wave-length and a given intensity.

An admirable illustration of this is to be found in the equilibrium between oxygen and ozone. At ordinary temperatures and under ordinary conditions ozone changes back slowly into oxygen and it is easy to convert several percent of the oxygen into ozone. At low temperatures the rate of decomposition is much less, and very much higher percentages of ozone can be obtained. With rising temperature, the rate of decomposition increases very rapidly and above 200° practically no ozone is formed by the silent discharge. All this is quite independent of any displacement of the straight chemical equilibrium due to ozone being an endothermal compound. So far as we know, this last is not an appreciable factor at any temperature.

[1] Zeit. phys. Chem., 51, 297; 53, 385 (1905).
[2] Ibid., 53, 404 (1905).
[3] Cf. Haber: Zeit. Elektrochemie, 11, 849 (1905).

Alexander Smith[1] has shown that hydrogen sulphide and ammonia accelerate the rate at which fused amorphous sulphur changes back into ordinary melted sulphur. Berthelot[2] states that no insoluble sulphur is formed when sunlight acts on a solution of sulphur in carbon bisulphide saturated with hydrogen sulphide gas. This statement is too sweeping, as a matter of fact; but the presence of hydrogen sulphide does decrease the amount of sulphur which can be converted into soluble sulphur by light. It has been shown by Mr. Rankin, in my laboratory, that the addition of ammonia gas to solutions of sulphur in other solvents than carbon bisulphide checks the production of insoluble sulphur by light.

The bearing of this on the phase rule relations is now clear. In cases of reversible equilibrium, light acts as another variable and $n+3$ phases are required for an invariant system. We have the varying intensity of light introducing another degree of freedom. Strictly speaking, we have as many degrees of freedom as we have kinds of active light; but for most purposes we can treat a beam of light as though it were homogeneous, provided we vary the intensities of the constituent rays uniformly. One case is already known and others will doubtless be discovered in which light of one wave-length and a given intensity produces a given equilibrium while light of another wave-length and the same intensity produces another equilibrium. If now we act on the system with a ray made of these two wave-lengths, and vary the relative intensities of the two monochromatic lights in the compound ray we shall introduce two degrees of freedom, and m degrees of freedom if we have m kinds of active monochromatic light, the relative intensities of which are independently variable. These, however, are refinements which will present no difficulties when the concrete cases arise. When the independent variables of a system are the n components, the pressure, the temperature, and m kinds of active light, $n+m+2$ phases constitute an invariant system. The

[1] Jour. Am. Chem. Soc., 27, 797, 979 (1905).

[2] Comptes rendus, 70, 941 (1870).

number of phases constituting an invariant system reduces to $n+3$ when dealing with absolutely monochromatic light or when the relative intensities of the m kinds of active light depend solely on the intensity of the composite ray.

For a given initial mass of oxygen at a given pressure and temperature, the equilibrium percentage of ozone is fixed, provided these are the only variables; but it is not fixed if we introduce ultra-violet light as an independent variable. For ultra-violet light of zero intensity, the equilibrium percentage of ozone is practically zero. For a given, though unknown, intensity, of ultra-violet light at 20° Regener[1] found an equilibrium percentage of 3.4 percent ozone. It is evident that any intermediate value could be obtained by using intermediate intensities of the ultra-violet light. In one case Regener obtained equilibrium with 2.2 percent of ozone, but it is not certain whether this variation was due to a decreased intensity of the ultra-violet light or to a change in its composition. For the present that is immaterial. The essential thing is that at constant pressure and temperature we get a dynamic equilibrium between oxygen and ozone and that this equilibrium varies with variations in the ultra-violet light.

Reference has previously been made in this paper to the fact that light of less than 200$\mu\mu$ converts oxygen into ozone while light of 200–300$\mu\mu$ changes ozone into oxygen. If we vary the relative intensities of these two kinds of light independently, we are introducing two new variables instead of one and $n+4$ phases constitutes an invariant system. The experiments of Regener were not made with this in mind, but they are sufficient to establish the proposition.

Since the rate of the reverse reaction increases with rise of temperature, we should expect to find less and less ozone at higher temperatures. Reference has already been made to the fact that practically no ozone is obtained above 200°. For what are presumably similar conditions of exciting light, Regener finds 3.4 percent ozone at 20°, 3.15 percent ozone at 40°, and 2.7 percent ozone at 54°.

[1] Drude's Ann., 20, 1041 (1906).

With oxygen and ozone, no solid and liquid phases can be obtained at any except very low temperatures. With sulphur, however, it would be a comparatively simple matter to realize a change of freezing-point with changing intensity of light. Berthelot[1] states that solid rhombic sulphur is not changed into soluble sulphur by light but this is obviously a case of experimental error. If insoluble sulphur precipitates pure from a solution, the nature of the solvent cannot affect the equilibrium between the rhombic and the insoluble sulphur. Berthelot was probably misled by the formation of a surface film which prevented further action. In the absence of light, insoluble sulphur is never a stable solid phase, though an instable quadruple point has been realized with monoclinic and insoluble sulphur in contact with vapor and melt. Under the influence of light, insoluble sulphur can be made the stable phase at ordinary temperature. By adjusting the intensity of the light, rhombic sulphur and insoluble sulphur may be made to coexist in stable equilibrium over a wide range of temperatures.

More interesting than this is the case of a solvent and a light-sensitive substance which occurs in two modifications in solution. Depending on the assumptions made as to the action of light, we can, of course, construct a number of solubility diagrams. Two instances will be sufficient to show the general method. As the simplest possible case we will postulate that neither modification affects the solubility of the other and that the action of light is to displace the equilibrium without affecting the solubility of either modification. There are then only two possibilities: that the light causes increased formation of the less soluble modification, or that it causes the formation of the more soluble modification. The isotherms for these two possibilities are given schematically in Fig. 1. The abscissas are solubilities of the light-sensitive substance and the ordinates are intensities of light. The curve ABC represents the case in which the less soluble

[1] Comptes rendus, 70, 941 (1870).

form is made stable by light while DEF is the reverse case. The point A is the solubility point as usually determined. With increasing intensity of light, there is an increased formation in solution of the other modification. At B the second modification precipitates and we have a quadruple point stable under the influence of light only. The curve

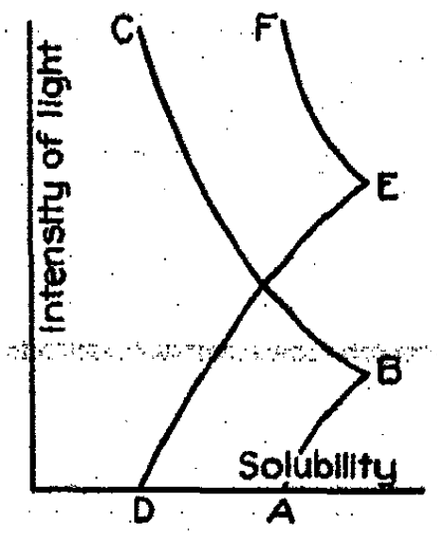


Fig. 1

AB is a straight line parallel to the axis of ordinates if the solubility of the second modification is zero. Along BC the second modification is solid phase. This curve can never pass to the left of a point representing a saturated solution containing only the second modification. The higher the rate of the reverse reaction, the farther to the right will C lie. If the solubility of the second modification is zero, the curve BC may approach the axis of ordinates asymptotically. The second case in Fig. 1 requires no special discussion. The points D, E and F correspond to the points A, B and C respectively. For extreme in solubility in the dark D would lie at the origin.

No case is definitely known in which light causes the formation of a more soluble modification, and Roloff[1] believes that no such case can occur. This seems to me an unjustifiable conclusion. We have already seen that certain wavelengths change oxygen into ozone and that certain others change ozone back into oxygen. There is no apparent reason

[1] Zeit. phys. Chem., 26, 345 (1898).

why this should occur only in cases where there is no measurable amount of one modification when the system reaches equilibrium in the dark. Yet if this limitation does not hold, we shall eventually find cases in which the solubility isotherm corresponds to the curve DEF in Fig. 1.

The curve ABC in Fig. 1 could doubtless be realized by studying the equilibrium between anthracene and dianthracene in a suitable solvent at a suitable temperature. The special case in which the second modification is practically insoluble, has been worked out in my laboratory by Mr. Rankin for sulphur and carbon bisulphide. The results obtained furnish a gratifying confirmation of the applicability of the phase rule classification to equilibria of this class.

Dutoit[1] has recently shown that the conductivity of halide salts dissolved in methyl ethyl ketone decreases when the solution is exposed to light. In a $n/622$ solution of sodium iodide, the value for μ was 84.9 in the dark and only 57.8 in bright sunlight. The action is reversible and the original conductivity is regained when the solution is put back in the dark. It seems possible that this change of conductivity might be accompanied by a change of solubility and it is to be hoped that this experiment may be tried.

This discussion leads up to a new way of looking at the equilibrium between CO, H_2O, CH_4, C_2H_2, etc. If the silent discharge or if ultra-violet light acted only as a catalytic agent, we should reach a final equilibrium which would depend solely on the percentage composition of the gas, provided the pressure and temperature were fixed. It would be entirely independent of the nature of the gases with which we started. For the simpler two-component, two-phase system of hydrogen in presence of an excess of carbon, Bone and Jerdan[2] found that at high temperatures the final equilibrium was the same whether they started with hydrogen, methane or acetylene. Such a result obviously does not open up much

[1] Zeit. Elektrochemie, 12, 642 (1906).
[2] Jour. Chem. Soc., 71, 59 (1897).

in the way of new fields for systematic work. We now see, however, that the equilibrium reached by means of ultra-violet light will depend on the nature and the intensity of the ultra-violet light. If certain substances contain specific absorption bands we can lessen the decomposition of these substances by using light which does not contain wave-lengths corresponding to the absorption bands in question. While the problem of photo-synthesis or plant-synthesis is admittedly not an easy one, the phase rule line of attack seems by far the most promising one.

Cornell University.

NEW BOOKS

La Théorie physique, son objet et sa structure. *By P. Duhem.* (*Bibliothèque de philosophie expérimentale*). *14 × 23 cm; pp. 450. Paris: Chevalier and Rivière, 1906. Price: paper, 8 francs; bound, 9.50 francs.*—Duhem's treatise on the object and structure of physical theory is a commentary on the thesis that a physical theory is a system of mathematical propositions deduced from a small number of principles, the aim of which is to represent as simply, as completely, and as exactly as possible an ensemble of experimental laws. Duhem rejects the view that the object of a physical theory is to explain such laws. For explanation is metaphysics, and no metaphysical system suffices for the construction of a physical theory.

Duhem maintains that a physical theory is constructed by (*a*) definition and measure of physical quantities, (*b*) choice of hypotheses, (*c*) mathematical development, (*d*) comparison with experiment. The use of the theory is to economize thought. The theory classifies experimental laws, and does this in a way so striking that the classification seems a natural and not an artificial one. In the history of physics, explanations have come and gone like the waves of the surf; but natural classification has advanced like the tide. Contrasting logical coordination with imaginative grasp, Duhem makes a brilliant comparison of French and German analytical methods with the predominantly English use of mechanical models.

The structure of physical theory is the subject of the remainder of the volume. Theoretical physics, to accord with Duhem's definition, must be a mathematical physics. A physical attribute may be denoted by a numerical symbol only when it is a quantity or a quality. The prime magnitudes to be coordinated by theoretical physics are those as yet irreducible. Experimental measurements being approximate, and mathematical statements being exact, a mathematical deduction is useful only when it yields a result that is measurable. To physical observation corresponds an approximation mathematics. Duhem concludes by a detailed examination of the implications of a physical experiment, the consequent nature of physical laws, and the evolution of the fundamental hypotheses that these laws suggest.

The above brief outline can give but a faint notion of the striking qualities of this book. From start to finish the argument is interesting, is systematically thought out, and is clearly stated; and every point made is adequately illustrated by a pertinent example. Simply written, and abounding in sound ideas and clever illustrations, it is an exceedingly interesting book.

J. E. Trevor

Introduction to General Inorganic Chemistry. *By Alexander Smith. 13 × 21 cm.; pp. xviii + 780. New York: The Century Co. 1906. Price: bound, $2.25 net.*—Among the many texts which the publishers hand to us from month to month, few of those in inorganic chemistry offer anything that is really new either in material or in point of view. The present work is an exception to the rule, for while the arrangement is very much the conventional one, the style

in which matters are discussed is decidedly individual, since the work is a distinct attempt at rational thinking about natural phenomena.

The text, though a large one, is intended for the beginner; but throughout, and especially in the earlier chapters, there are many paragraphs in smaller type intended for the profit of more mature students who may use the book. It is in these paragraphs, where the author feels free to digress a little and to speak out on the subject in hand, that the bent of his mind is revealed. His desire is very great for an exact phraseology, and when he passes in review our ordinary expressions, he is able to find that almost every one of them either means the opposite of what it says, or at any rate fails to express the idea it was formed to convey. He thus often becomes a paradox hunter: "We know of no causes, in the sense in which the word is commonly employed" (p. 30). We may not speak of the gas as "disobeying" Boyle's law, because it is the law which is really imperfect, and not the gas, the proof of which is that we do not attempt to discipline the gas, but merely modify the law (p. 8). Of course the expression "affinity" comes in for its share of punishment, and the "loves of the elements" are shown up for the imaginary things we knew they were.

The author goes too far in arguing that because the only first-hand knowledge we possess is that of our states of consciousness, therefore energy and matter do not exist as objective realities. There is always the chance that we may have had luck and hit upon the truth in assuming them.

Despite this passion for accuracy, the book is not free from inaccuracies. Thus, we find—"boiling point (temperature above which at 760 mm. pressure the substance is gaseous)" on p. 35; and "boiling point (temperature of vaporization)" on p. 37. The phrases in brackets are apparently meant as explanatory to the term *boiling point*, and if so they leave much to be desired. Also one would fain ask why the phrase "molar weight" is preferred to "molecular weight" in the statement on p. 262 that isomers may have equal molar weights or they may have different molar weights, especially since it is made clear on p. 197 that a molar weight is a gram-molecular weight.

A most misleading expression appears on p. 52,—"Pressure is the special name for concentration in gases." Why not as well temperature? or volume? And is osmotic pressure then the special name for concentration in solutions?

There are many such trifles in the text that one could quarrel with; but all this petty fault-finding serves only as a background for the praise which must be freely accorded to the work in its main features. The material is well selected, and of course complete in a work of this size; the treatment is careful to a fault, very modern in spirit, and in general accurate; but, best of all, the book is good reading; instructor as well as student will profit by its study. It is one of the few elementary texts that should be in the hands of every teacher. Whether it will be a success in the class-room only time and trial can show, but its chances should be very good, and if one dared predict success for a textbook one would do it for this. At any rate the publishers are already loading testimonials of its usefulness upon us. It does not seem adapted to short courses, but is well designed for the advanced student, or for the beginner where the allowance of time is ample.

A. P. Saunders.

Physical Chemistry for Electrical Engineers. *By J. Livingston R. Morgan. 12 × 19 cm; pp. v + 230. New York: John Wiley and Sons, 1906. Price: cloth, $1.50.*—This little book, made for a special audience, is on the whole well designed for its purpose, and should be useful. Its purpose is "to present, in as popular a form as is consistent with quantitative results, those laws and generalizations of physical chemistry which form the basis of the subject embracing the chemical application of electricity and the electrical application of chemistry." (p. IV.)

The author has purposely avoided the use of any hypotheses in his treatment, feeling, as he says, "that by placing the subject upon an absolutely experimental basis . . the reader's idea will be more clear and scientific." (p. V.) But the attempt to construct a textbook in a science without making use of the hypotheses which have been evolved to light the dark ways, is very much like throwing away one's lantern when lost in the woods.

Of course without hypotheses we cannot speak of atoms or molecules, and the result of this is the constant reappearance of the cumbrous phrases "combing weight" and "formula weight" in their place, a result confusing to the mind of any one accustomed to the simpler terms. Even the author himself fails to keep the sense of these expressions clear in his mind, and speaks on p. 7 of "2 formula or combining weights of hydrochloric acid." This attempt to dispense with hypothesis is all the more useless since the book could not possibly be used by any one who had not studied at least enough chemistry to have become familiar with the terms *atom* and *molecule*.

Not only a familiarity with elementary chemistry but some acquaintance with the calculus will be necessary to those who wish to use the book.

Minor blemishes appear here and there; students fall of themselves only too easily into the use of such slipshod expressions as "74 cm. Hg pressure" (p. 221) and an author should be careful not to imitate them. On p. 45, we find the statement: "The transformation of heat into work takes place only through the medium of a gaseous body," an extraordinary statement, surely. And on p. 172 a questionable use of the word *regulate* in the phrase, "Faraday's law, which regulates the relationship between the quantity of electricity flowing and the amount of substance it deposits."

The references for further information, besides some to the original articles, are entirely to the author's "Elements;" it would have looked better, and perhaps been a convenience to some, if other texts had also been indicated.

Misprints are rare, but the alignment on some pages (*e. g.*, p. 88) is so bad as to cause discomfort in reading. There is no index.

One of the excellencies of the book is a set of 78 problems at the end, which will serve as a most useful drill for the student. *A. P. Saunders.*

Vorlesungen über anorganische Chemie für Studierende der Medizin. *By Ernst Cohen and P. van Romburgh. 17 × 24 cm; pp. iv. + 428. Leipzig: Wilhelm Engelmann, 1906. Price: paper, 15 marks.*—Water is the subject taken up in the first lecture; oxygen is reached in the sixth lecture, and hydrogen in the seventh. There are thus practically five introductory lectures. The sub-heads will give an idea of what these lectures contain. Water, solution, filtration, distillation, solubility, decomposition of water, reactions, reaction velocity,

catalysis, mixtures and compounds; quantitative relations, conservation of mass, elements, synthesis, law of definite proportions, law of multiple proportions, atomic hypothesis, atoms and molecules, molecular weight, symbols, table of atomic weights, chemical equations, percentage composition of water, vapor density, analysis of water, vapor density determinations; crystals, reversible changes, inversion temperature, sublimation, freezing-points of solutions, electrical disintegration, dialysis, crystalloids and colloids, lowering of the freezing-point; electrolytic dissociation, acids, strength of acids, bases, strength of bases, formation of salts, acidimetry and alkalimetry, titration; heat effects, law of constant heat effect, dissociation of gases, chemical equilibria, hygroscopic substances, solubility of gases, Henry's law.

It will be noticed that the student gets quite a little straight physical chemistry at the very beginning. As thus presented, it seems distinctly a good thing. In fact the whole book is a carefully written one, even to the extent of always saying "practically insoluble" when speaking of barium sulphate, silver chloride, etc. This may seem pedantic to some, but it is needed. The book contains sixty-eight half-tone illustrations, almost all of them admirable.

Wilder D. Bancroft.

Abriss der allgemeinen oder physikalischen Chemie. *Als Einführung in die Anschauungen der modernen Chemie. By Carl Arnold. Zweite verbesserte und ergänzte Auflage. 13 × 20 cm; pp. viii + 228. Hamburg und Leipzig: Leopold Voss, 1906. Price: bound, 375 marks.*—This work has already been noticed in the columns of the *Journal* (9, 159), and there is little to add to the remarks there made about it.

It represents what we may call the compressed food pellet type of book; and may prove healthful for those who can nourish their minds on pure truth without any waste matter. And yet not pure truth either, for lapses from strict accuracy are not infrequent, as a reading of the chaper on solutions will show.

It is not exhaustive enough to use as a work of reference, and yet too exhausting to serve as a textbook. But it does cover the ground in only a little over 200 pages.

A. P. Saunders

Grundriss einer Entwicklungsgeschichte der chemischen Atomistik, zugleich Einführung in das Studium der Geschichte der Chemie. *By Richard Ehrenfeld. 19 × 23 cm; pp. viii + 314. Heidelberg: Carl Winter's Universitätsbuchhandlung, 1906. Price: paper, 8 marks.*—Serviceable books on the history of chemistry are so few that one must welcome every addition to the ranks. The present volume gives an account of only one side of the science, the theoretical. From the Greek philosophers to Ostwald and J. J. Thomson, the progress of thought regarding the nature of the atom is traced. To many readers it will seem that an undue amount of space is given to the ancient speculations on the structure of matter, considering that they had no connection with an organized experimental science; and the same may be said of the theories of the alchemists. With the advent of Robert Boyle, of whose great influence the author is fully appreciative, the theoretical side of the science gets a more solid foundation, and from that point onward the work gains immensely in interest.

Such a treatise, from the very nature of its subject-matter, appeals to a rather small audience; and among English-speaking chemists the numbers

will be further reduced by the fact that the work is written in a style which is far from easy, and which at times soars into the realms of "fine writing." But for those who will take the trouble to read it, the work contains a great deal that is valuable, and brings the matter up to within about a year of the present date. The later chapters are particularly useful, since they gather together the ideas that have been suggested by Ostwald, Ernst Mach, Wald, and others, regarding the fundamental chemical laws and the constitution of matter,—ideas which have developed under the influence of the results obtained in the field of radio-activity on the one hand, and on the other hand under the guidance of the phase rule, which has given to chemistry a basis less subject to hypothesis and more far-reaching than the atomic and molecular theories could provide. *A. P. Saunders*

Thermodynamique. II. *Introduction à l'Étude des Machines thermiques. By L. Marchis. (Bibliothèque de l'Élève Ingénieur.) 16 × 25 cm; pp. 255. Grenoble: A. Gratier and J. Rey. Paris: Gauthier-Villars, 1905. Price: paper, 5 francs.*—This is the second volume of a textbook on thermodynamics, intended for the use of students of engineering. The first volume, on the principles of thermodynamics, was noticed in this Journal, 8, 576. The second volume is a short treatise on the thermodynamics of one-component fluids. It treats the subject in two chapters, one of which is concerned with the specific volume, specific heats, heats of combustion, and changes of the thermodynamic state, of ideal gases; and the other, on saturated vapors, with vapor-pressure, heat of evaporation, the specific volumes and specific heats of saturated liquid and vapor, changes of the thermodynamic state of the two-phase system liquid-vapor, and the neutral curve. The treatment is satisfactory enough; but the typography of the book is most unpleasing. *J. E. Trevor*

Space and Geometry in the Light of Physiological, Psychological and Physical Inquiry. *By Ernst Mach. 14 × 20 cm; pp. 148. Chicago: The Open Court Publishing Co., 1906. Price: cloth, $1.00.*—Through the consideration that our notions of space are rooted in our physiological organism, that geometric concepts are the product of idealization of physical experiences, and that systems of geometry arise from the logical classification of the conceptual material thus obtained, Mach makes it plain that psychology, physics, and logic must all be drawn upon for effective epistemological inquiry concerning space and geometry. In the present little volume he makes use of all these different points of view in a discussion of the origin, development, and nature of geometry. The result is a broad and sensible view of the matter. It is not easy reading; but it is unquestionably worthy of the most serious attention. *J. E. Trevor*

Müller-Pouillets Lehrbuch der Physik und Meteorologie. *Herausgegeben von Leop. Pfaundler. In vier Bänden. Zehnte umgearbeitete und vermehrte Auflage. Erster Band: Mechanik und Akustik; von Leop. Pfaundler. 16 × 25 cm; pp. xiv + 801. Braunschweig: Friedrich Vieweg und Sohn, 1905. Price: paper, 10.50 marks.*—Since the German *Gymnasien* send their students to the university without any training in the higher mathematics, there arises in Germany, on the part of students for whom physics is an auxiliary science, an extensive demand for a handbook from which such students can get a useful grasp of

physics from its experimental side. Such a handbook the present work, now in its tenth edition, is intended to provide. With the aid of a number of competent collaborators, the editor plans to complete the edition so promptly that the whole work shall be available before any part of it will have fallen seriously behind the times. From the manner in which the first volume, on mechanics and sound, has been executed, there is every reason to anticipate that the "Müller-Pouillet" will continue to fill the useful place that it has long honorably occupied.

J. E. Trevor

Traité de Physique. *By O. D. Chwolson. Ouvrage traduit sur les Éditions russe et allemande par E. Davaux. Édition revue et considerablement augmentée par l' Auteur, suivie de Notes sur la Physique théorique par E. Cosserat et F. Cosserat.*

Tome premier, second Fascicule: 16 × 25 cm; pp. iv + 559.

Tome deuxième, second Fascicule: 16 × 25 cm. pp. viii + 431.

Paris: A. Hermann, 1906.—The French edition of Chwolson's treatise on physics is continued by the issue of the second parts of the first and second volumes of the work. These parts treat the gaseous state of bodies, and index of refraction, dispersion, and transformations of radiant energy, respectively. The scope and character of the treatment have been sufficiently outlined in previous notices (see 10, 303).

J. E. Trevor.

Populäre Schriften. *By Ludwig Boltzmann. 14 × 22; pp. iv + 440. Leipzig: Johann Ambrosius Barth, 1905. Price: bound, 9 marks, paper, 8 marks.*—Although the twenty-three popular articles and addresses of Boltzmann collected in this volume are for the most part very well known, it is a convenience to have them gathered from the scattered sources and brought between two covers. In making the collection, the term Popular Writings is construed in a liberal sense, for it is made to cover not only compositions addressed to the general educated public, such as the brilliant memorial addresses on Kirchhoff, Stefan, and Loschmidt, expositions of various special topics of theoretical physics and of allied questions in epistemology, and the impressions of a recent trip to California, but also articles of a distinctly technical nature, such as those contributed to the discussion of a decade ago on the energistics of Ostwald and Helm, and formal academic lectures on the methods of theoretical physics and on the principles of mechanics. Most of these writings are of recent dates, nearly all of them having appeared within the last ten years. At the present time nothing in the collection retains more interest and importance than the five controversial articles of 1896 and 1897 on the subject of energistics. These papers are to be commended to the study of those who still follow Ostwald in this matter.

J. E. Trevor

Cours de Physique de l'École Polytechnique. *By J. Jamin. Troisième Supplément: Radiations; Électricite; Ionisation. By M. Bouty. 14 × 23 cm; pp. vi + 419. Paris: Gauthier-Villars, 1906. Price: paper, 8 francs.*—The issue of a third supplement to Jamin's *Cours de Physique* brings this standard work up to date in the matters of radiation, electricity, and ionization. Much of the text, of course, has a purely physical interest. But the chapters on electrolysis are interesting for physical chemistry in that they constitute an admirable brief treatise on electrochemistry; and the presentation of radioactivity

will appeal to a wide audience. The reputation of the author is sufficient guarantee of the excellence of the work. *J. E. Trevor*

Einführung in die Thermodynamik auf energetischer Grundlage. *By Julius Meyer 17 × 24 cm; pp. viii + 216. Halle: Wilhelm Knapp, 1905. Price: paper, 8 marks.*—The author describes this book as an attempt to present thermodynamics and its results in the most tangible manner. The manner chosen is that of Ostwald's energistics, the hypostasizing of energy. That this very metaphysical method is the most tangible may be doubtful, but there is little room for doubt that it is very unsuitable. The book contains much the usual matter of elementary treatises on thermodynamics; but, in the opinion of the reviewer, its vicious method and superficial execution preclude it from being really useful to anybody. A book of this kind worries a capable student, and tends to give a thoughtless one the false idea that he comprehends it. In each case the student's mind is confused and his time is wasted. *J. E. Trevor.*

Volume and Surface Integrals used in Physics. *By J. G. Leathem. (Cambridge Tracts in Mathematics and Mathematical Physics, No. 1.) 14 × 21 cm; pp. 47.*

The Integration of Functions of a Single Variable. *By G. H. Hardy. (Cambridge Tracts in Mathematics and Mathematical Physics, No. 2.) 14 × 21 cm; pp. vi + 53.*

London: Cambridge University Press, 1905. Price: paper, 2s. 6d. net, each.

The two "tracts" above described inaugurate a series that is apparently intended to elucidate topics that one cannot expect to find adequately treated in current textbooks. The first tract is concerned with the volume and surface integrals that are constantly met in the study of electricity and the theory of attractions. It examines how far it is justifiable to represent by such integrals the potential and other physical quantities associated with a body that is supposed to have molecular structure; and it gives proofs of certain mathematical properties of these integrals, which one is likely to assume as obvious though they are not. Illustrations are taken from physical theory, and only the difficulties that present themselves in physical applications are considered. The second pamphlet is a supplement to the usual accounts of indefinite integration. An effort is made to show that the process of this integration is not really a bag of tricks, but that the solution of any elementary problem of integration may be sought in a definite and systematic way, and that the "tricks" find their place in the general theory. *J. E. Trevor*

Elektron. *Der erste Grundstoff. By J. R. Rydberg. 17 × 25 cm; pp. 30. Berlin: W. Junk, 1906. Price: paper, 1 mark.*—In the arrangement of the elements in the periodic table, the author recognizes a period of two places between successive elements of even or of odd valence, a second period of eight places determining the "valence group," and a third period of eighteen places determining the larger period. This leads him to represent the ordinal number M of the elements as depending linearly on three variables x, y, z, each representing the current integers,

$$M = 2x + 8y + 18z + v,$$

where the term v determines the valence and may be made zero or unity. So, for the ordinals for the elements of even and of odd valence,

$$M = 2x + 8y + 18z$$
$$M = 2x + 8y + 18z + 1.$$

Putting, for these successive cases, $M = 2m$, $M = 2m + 1$, the equations take the common form

$$m = 1^z.x + 2^z.y + 3^z.z.$$

Computing the M's by means of this equation, and arranging the results with reference to rectangular coordinates, the author obtains a cubical pile of points (blocks) for the elements of even valence, and a like pile for the elements of odd valence. All this, of course, is merely an arrangement of the integers such that their successive differences in an xy-section of the pile are 2 and 8, in an xz-section 2 and 18, and in a yz-section 18 and 8.

The substance of "electrons," of atomic weight nearly zero, is taken to be the element corresponding to the position M = 0 in the table; and the significance of this assumption, for chemistry, physics, and astrophysics, is extensively discussed. *J. E. Trevor.*

Kurzes Repetitorium der organischen Chemie. *By Kurt Dammann. 11 × 20 cm; pp. xiii + 256. Freiburg: Herdersche Verlagshandlung, 1906. Price: bound, $1.25 net.*—This book is intended primarily for students reading up for an examination and is more compact even than the corresponding Bernthsen book. There is an excellent index and there is no reason why the volume should not fulfil its purpose. Whether its purpose is a desirable one is a matter of purely academic interest. There is certainly a sale for such books in Germany. *Wilder D. Bancroft*

Amerikanisches Hochschulwesen. Eindrücke und Betrachtungen. *By W. Böttger. 16 × 24 cm; pp. 70. Leipzig: Wilhelm Engelmann, 1906.*—Dr. Böttger was a research associate for a time in the Research Laboratory of Physical Chemistry of the Massachusetts Institute of Technology. In this little pamphlet he records his first impressions on arriving at New York and then gives a careful analysis of university conditions in this country. The book is written for a German audience, but there will probably be many in this country who will be interested in glancing over the pages. *Wilder D. Bancroft*

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