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ON IRREVERSIBLE CELLS.

BY A. E. TAYLOR.

The present paper is a continuation of the work of Bancroft[1] on single-liquid polarizable cells, with especial reference to the effect of the negative ion on the potential difference between an electrode and the electrolyte in which it is immersed. The electromotive force of a cell, having for electrodes any two of the metals Mg, Zn, Cd, Sn, Pb, or Bi in solutions of chlorides, bromides, iodides, sulphates, nitrates or acetates, does not seem to be in any way a function of the negative ion. When, however, mercury serves as one electrode a variation with the negative ion always appears. Measurements were made with zinc and cadmium in combination with mercury in chloride, bromide, iodide, nitrate, sulphate and acetate solutions. The results obtained were compared with the values given by Paschen[2] for the single potential differences entering into these same cells. The measurements of Paschen show in every case a variation with the negative ion for the single potential difference. That these variations do not appear in the electromotive forces of the cells in which two of the metals Mg, Zn, Cd, Sn, Pb or Bi are used as electrodes, is explained by the fact that for each negative ion the term due to it has the same numerical value and the same sign for each metal, but varying for the different ions. So, in the electromotive force, which is the sum of the two potential differences taken in opposite directions, this term due to the negative ion disappears. With mercury, however, the value of the term seems to be the same as with the other metals mentioned but with opposite sign. In consequence of this difference in sign, there appears in the electromotive force of a cell, in which mercury is one of the electrodes, a term due to the negative ion and having a value equal to

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[1] Zeit. phys. Chem., **12**, 289 (1893); Physical Review, **3**, 250 (1896).

[2] Wied. Ann., **43**, 590 (1891).

twice that appearing in the single potential differences. With platinum the numerical value of this term is no longer the same. The behavior of copper, in this respect thus becomes a matter of interest, and the first part of this paper is given to an investigation of cells composed of Zn, Cd, Hg and Cu in solutions of chlorides, iodides and sulphates.

The cadmium first used was taken from the University museum and later some pure cadmium was obtained from Eimer and Amend. Measurements made with the various cadmium electrodes on the cell, Cd|chloride|Hg all agreed very well among themselves, and further agreed with the measurements of Bancroft on the same cell. Two sticks of pure copper, previously used by Prof. Bancroft in electrical measurements, served as copper electrodes. The mercury used was purified according to the method given by Ostwald in his *Physiko-chemische Messungen*, *p.* 100, and gave extremely satisfactory results. Impure mercury was repeatedly shaken with dilute sulphuric acid to which was added a few drops of potassium bichromate, and after being carefully washed with distilled water, was allowed to run in a fine stream through a long column of ten per cent. nitric acid. This last process was repeated several times. The pure mercury finally obtained retained a perfectly bright surface during a period of several months, in fact until it was all used. Especial care was exercised in the preparation of the potassium salts used. The potassium chloride had been prepared by being six times precipitated from a concentrated solution of the salt by hydrochloric acid gas, and had been previously used to determine the constant of a conductivity cell. It had also been compared with potassium chloride used by Dr. Kortright in conductivity work, and in both cases the same constant was obtained for the cell. The sulphate first used probably contained a trace of some other salt for it gave low values; but on being recrystallized several times very satisfactory results were obtained.

The determinations of the electromotive force were made with a small Lippmann's electrometer according to the well known compensation method of Poggendorff. A Latimer Clark cell served as a normal element. This cell was compared from time to time with another Clark cell, and the two were always found to agree within at least a millivolt. Two Leclanché's having a combined electromotive force of about 2.6 volts were used as a working cell. These cells were very constant, although they slowly changed to the extent of about three or four per cent. The value of the Clark in terms of the Leclanché was determined two or three times a day.

The single-liquid cells measured were made up in little vials of about twenty-five millimeters in diameter and seventy-five millimeters in height. These vials were provided with paraffined corks into which the electrodes were tightly fitted. In case that mercury was used as one of the electrodes, a glass tube, into which a platinum wire had been fused, passed down through the electrolyte and made connection with the mercury. Great care was taken to keep the cells perfectly clean, as slight impurities have a very marked effect. Whenever the cells were made up they were first very carefully washed for a long time with distilled water; and each time, the electrodes were carefully scraped or cut with a sharp knife to ensure a bright clean surface, then washed with distilled water and wiped with filter paper to remove any loose particles of metal. The bottles used for the solutions were first thoroughly washed with distilled water and then boiled out with steam.

In all cases the maximum reading of the electromotive force of the cell was taken, for all the cells measured were found to increase rather quickly to a maximum, which remained constant for a time. Most of the cells reached a maximum reading in about an hour, while some of the cells, especially the sulphate cells, might require two or three hours. In a few cases the maximum was reached in fifteen or twenty minutes. However, the time for any particular cell was not in the least constant. Throughout this whole paper twentieth normal solutions are always used when no concentration is specified.

The cells first measured were potassium chloride cells in which Cu, Hg and Cd served as electrodes.

The cells are all measured in volts, the value of the standard Clark being taken as 1.434 volts at 15°C. Each value represents a different cell, a series of readings being taken, and the maximum which remains constant being given. The cells are always written,

TABLE I.

—n/20 K Cl—

Electrodes	Cd | Hg	Cu | Hg	Cd | Cu
	0.821	0.255	0.546
	0.814	0.251	0.568
	0.815	0.254	0.566
	0.812	0.254	0.568
	0.813		0.568
	0.818		0.561
			0.557
Averages ...	0.815	0.253	0.565

e. g., Cd | $\frac{n}{20}$ KCl | Hg, so that the current in the cell runs from left to right, the anode thus being written first. A list of measurements is given rather than a simple average, in order that the variation of the various cells may be seen. A greater accuracy than 0.01 volts is not claimed for the results, although it seems probable that the accuracy is somewhat greater than that. It will be seen that the cells obey very well Poggendorff's law, in that the value of the cell Cd | Hg is very nearly equal to the sum of the values given for the two cells Cd | KCl | Cu and Cu | KCl | Hg. It would seem therefore that the averages give values which differ but a few millivolts from the true values of the cells measured. At any rate the maximum variation observed would have little or no effect upon the general facts observed.

The sulphate cells in table II were measured.

The values of these cells were much harder to determine than the corresponding ones for the chloride cells. The slightest impurity has a very large effect. A great many measurements were made with a sulphate solution, which I supposed to be pure. The results, however, did not agree very well among themselves, nor would they add up according to Poggendorff's law. The cell Cd | Hg was not equal to the sum of the two cells Cd | Cu and Cu | Hg. The salt was thereupon purified by repeated crystallization and satisfactory measurements were obtained. A very slight amount of sulphuric

TABLE II.

—n / 20 K_2SO_4—

Elec-trodes	Cd | Cu	Cu | Hg	Cd | Hg	Zn | Cu	(W.D.B) Zn | Cd	Zn | Hg[1]
	0.740	0.309	1.037	1.053		
	0.734	0.314	1.037	1.065		
	0.725	0.303	1.029	1.076		
	0.725	0.292	1.033	1.071		
	0.725	0.300	1.034	1.054		
	0.731	0.300	1.038	1.049		
	0.716	0.318	1.042	1.048		
	0.722		1.020	1.077		
				1.068		
				1.056		
				1.046		
				1.065		
				1.072		
				1.044		
				1.055		
Averages	0.727	0.306	1.034	1.061	0.334	1.367

acid was found to raise the value of the sulphate cells very considerably. The sulphate solutions used showed no trace of acid, when tested with a drop of phenol phthalein indicator, for the solution immediately turned red when a drop of very dilute potassium hydrate solution was added.

The following table for Cd, Zn, and Hg in halogen and sulphate solutions is given by Bancroft:

TABLE III.

Electrodes	K Cl	K Br	K I	K_2SO_4
Zn | Hg	1.151	0.991	0.847	1.302
Cd | Hg	0.818	0.659	0.515	0.969
Difference	0.333	0.332	0.332	0.333
Zn | Cd	0.333	0.333	0.331	0.334

The value 0.818 volts for Cd | KCl | Hg agrees very closely with the value 0.815 volts which I obtained. For the cell Cd | KI

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[1] Calculated from Zn | Cu + Cu | Hg, or from Cd | Hg + Zn | Cd.

|Hg I obtained 0.514 volts. My values for the sulphate cells do not agree at all with those obtained by Bancroft; but in view of the special care taken with these cells, it seems probable that his values are too low. I obtained lower values than Bancroft with the first impure sulphate solution used. The electromotive force, 1.367 volts which is given for the cell Zn | K_2SO_4 | Hg was not directly observed by me, but was calculated by the method indicated. The value given by several investigators is about 1.300 volts, but I think that the true value is probably higher. The cell is a very difficult one to measure, for it seems to polarize almost immediately. I observed about the same electromotive force 1.3 volts myself, but the cell did not remain constant at all and in a minute or two had fallen in value considerably, so that the true value must of necessity be higher than that first observed, and is probably not very different from the one calculated. Aside from the cell just mentioned, the cell Zn | K_2SO_4 | Cu was the most unsatisfactory one measured, in that the variations are very large; but from a large number of observations a fairly accurate mean value seems to be obtained.

Bancroft found cells of this kind to vary in no case with the concentration. My measurements confirm his results with the cell Cd | KCl | Hg and further I found the same thing to hold true of the cell Cu | KCl | Hg.

TABLE IV.

Electrodes	Electrolyte	Concentration	E. M. F.
Cd Hg	K Cl	n / 10	0.818
Cd Hg	K Cl	n / 100	0.817
Cd Hg	K Cl	n / 1000	0.819
Cu Hg	K Cl	n / 20	0.252
Cu Hg	K Cl	n / 400	0.253
Cu Hg	K Cl	n / 4000	0.251

The same thing holds true of all the cells as far as tried, so that two points with regard to these cells may be considered as fairly well settled; the concentration has no effect, and in every case the negative ion of the salt solution has an effect on the electromotive force of the cell.

Now these inconstant cells correspond somewhat closely to the values obtained from the two liquid reversible cells of the Daniell's type, as was first mentioned by Oberbeck and Edler, and further confirmed by the measurements of Bancroft. It would seem, therefore that these one-liquid cells might be considered as limiting cases of the two-liquid reversible cells. According to Nernst the potential difference between a metal and a solution of a salt of that metal is given by the formula[1]

$$\pi = \frac{RT}{ne} \log \frac{P}{p} \times 10^{-4} \textit{volts}$$

where π is the potential difference, n the valence of the cation, and p its partial osmotic pressure in the solution, P the solution pressure of the electrode metal and e the quantity of electricity carried by one gram equivalent. The electromotive force, E, of a cell $M_1 | p_1 M_1 X | p_2 M_2 X | M_2$, of the Daniell's type will be given by the expression

$$E = \frac{RT}{ne}\left(\log \frac{P_1}{P_2} + \log \frac{p_2}{p_1}\right) \times 10^{-4} + Z \textit{ volts}$$

where Z denotes a possible potential difference between the two solutions; and the valence of the two electrode metals is taken as being the same. Now if we take the two solutions of the same concentration, then the values of p_2 and p_1 are equal, if the salts are wholly or equally dissociated, and the term p_2/p_1 disappears. The electromotive force of the cell then becomes independent of the absolute concentration, if the term Z becomes negligible as is the case when the migration velocities of the ions M_1 and M_2 are equal. Under these conditions the electromotive force of the cell $Zn | ZnSO_4 | CuSO_4 | Cu$ has been found to be independent of the absolute concentration of the zinc and copper sulphates.[2]

Bancroft looks upon the one liquid polarizable cells as limiting cases of this cell. If both solutions in the cell are diluted with water, the electromotive force remains unchanged. Now according to Nernst's views, if we dilute with potassium sulphate solution instead of water the electromotive force would also be unchanged,

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[1] Zeit. phys. Chem. 4, 148 (1889).

[2] Wright, Phil. Mag., [5], 13, 265 (1882).

except as it is affected by any change of dissociation of the two sulphates. By increasing the amount of potassium sulphate we should finally reach the limit where the concentration of the zinc sulphate and the copper sulphate would be zero or, in other words, the cell $M_1|K_2SO_4|M_2$. Thus the one liquid polarizable cell $M_1|RX|M_2$ may be looked upon as the limiting case of the reversible two liquid cell $M_1|pM_1X|pM_2X|M_2$. The term Z is thereby eleminated and the migration velocities of the ions no longer have an effect on the cell. The difficulty of measurement brought about by polarization much more than counterbalances the slight error introduced in the term Z, and in the term $log\ (p_2/p_1)$. Table V gives some of the results obtained for both polarizable and reversible cells.

Most of these figures are taken from the tables given by Bancroft.[1] In the first four columns are measurements on single-liquid polarizable cells by Paschen[2], Bancroft[1], Oberbeck and Edler[3], and Ostwald.[4] The measurements of Ostwald are with free acids and give higher values. The next three columns are for reversible cells by Wright and Thompson[5], Neumann[6] and Braun[7] and in the last column several measurements by myself. The agreement is not good, but points to the fact that the irreversible cells are limiting cases of the reversible cells. This will be seen best in the cases where there is no insoluble salt formed in the reversible cells, that is, where the concentration is the same on both sides.

The Zn|Cd, Cd|Cu sulphate and Zn|Cu sulphate cells differ very little whether polarizable or reversible.

Ostwald,[8] however, seems to consider these polarizable cells as having no definite electromotive force, and to depend upon the concentration of the ions of the electrode metal which have gone into

[1] Proc. Am. Acad. **31**, 96 (1894); Physical Review **2**, 250 (1895).
[2] Wied. Ann. **43**, 590 (1891).
[3] Ibid. **42**, 209 (1891).
[4] Zeit. phys. Chem. **1**, 583 (1887).
[5] Phil. Mag. [5] **19**, 1 (1885).
[6] Zeit. phys. Chem. **14**, 193 (1894).
[7] Wied. Ann. **16**, 575 (1882).
[8] Lehrbuch, 2d Ed. **2**, 815-816.

TABLE V.

Electrodes	Electrolytes	Paschen	W. D. B.	O. & E.	Ostwald	W. & T.	Neumann	Braun	A. E. T.
Zn | Cd	Chloride	0.296	0.333	0.368	0.360	0.330	0.329	0.334	
Zn | Cd	Bromide	0.293	0.333	0.364	0.340	0.315		0.256	
Zn | Cd	Iodide	0.298	0.331	0.365	0.304	0.322		0.262	
Zn | Cd	Sulphate	0.350	0.334	0.430	0.401	0.360	0.362	0.33-37	
Zn | Pb	Chloride	0.512	0.526	0.561	0.610	0.591	0.598		
Zn | Pb	Bromide	0.525	0.528	0.541	0.599	0.571			
Zn | Pb	Iodide	0.545	0.527	0.558	0.587	0.455			
Zn | Pb	Sulphate	0.525	0.527	0.502	0.592	0.50-55			
Cd | Pb	Chloride	0.216	0.195	0.192	0.249		0.269		
Cd | Pb	Sulphate	0.18	0.194	0.17	0.191				
Cd | Cu	Sulphate				0.672	0.752	0.747	0.740	0.728
Zn | Cu	Sulphate				1.07	1.11	1.109	1.1	1.061
Zn | Hg	Chloride	1.112	1.151		1.173	1.12-26			
Zn | Hg	Bromide	0.983	0.991		1.036	0.972			
Zn | Hg	Iodide	0.846	0.847		0.841	0.801			
Zn | Hg	Sulphate	1.300	1.302		1.484	1.46-51			
Cd | Hg	Chloride	0.816	0.818	0.755	0.813	0.812			0.815
Cd | Hg	Bromide	0.670	0.659	0.632	0.696				
Cd | Hg	Iodide	0.548	0.515	0.465	0.535				0.514
Cd | Hg	Sulphate	0.968	0.969	0.962	1.083				1.034

the solution. This concentration might vary greatly with circumstances. Warburg[1] has shown, especially in certain cases, that air dissolved in the electrolyte will cause the electrode metals to go into solution, and that there may be observed a potential difference between a metal immersed in an electrolyte free from air and the same metal immersed in the same electrolyte containing dissolved air. So, it is usually said that these cells have no definite electromotive force as the concentration of the ions would vary with the amount of air dissolved or some other disturbing influence. However, I do not think it to be actually the case that a definite value cannot be obtained for these cells, as the measurements given seem to show a perfectly definite value. In general, the measurements of Oberbeck and Edler on the polarizable cells agree fairly well with those of Bancroft, though in some cases there are rather large variations. I think that these descrepancies between the measurements of different men are better explained in other ways. It is a well known fact that slight impurities in the electrodes used will alter the electromotive force very greatly. Further, it seems to be essential that the electrolytes used should be absolutely pure, that is, free from the salt of any other acid, more especially in the cases where the negative ion appears to have an effect. With sulphates the presence of any impurity is especially noticeable, and a glance at the table will show that the largest differences are with the sulphates. With the bromides I found that the addition of a slight amount of chloride raised the value, but that the effect of impurity was not as great as with the sulphate.

Bancroft gives a long list of measurements with the cell Cd| KCl|Hg, and the variations are comparatively small. With this cell, especially, there is no doubt about its having a perfectly definite value, since everyone finds nearly the same value for it. Take for instance the cells Zn/Cd where the E. M. F. is independent of the negative ion of the electrolyte. The values of Oberbeck and Edler for the chloride, bromide and iodide are regularly 0.03 volts higher than those of Bancroft. Among themselves the results of each investigator agree within four millivolts. Now, this is not what one

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[1] Wied. Ann. **38**, 321 (1889).

would expect if the air dissolved in the electrolyte explained the differences, but it is exactly what would be expected if the electrodes used by the two were not exactly alike. Bancroft obtained measurements which seem to be constant, and they conform surprisingly well to Poggendorff's law. All the results given in the above table for zinc and cadmium with mercury vary but little.

I think that the action of oxygen on the electrodes does sometimes explain the variations of the individual investigator. Warburg finds that with zinc and copper the effect of air is especially large and somewhat variable. It was exactly with Zn|Cu cells that I found the largest variations for any particular cell, as is well shown by my Zn|K_2SO_4|Cu cell. Further the values for reversible cells, given by different investigators do not agree any too well, and here slight impurities in the materials used is the only explanation, if care has been used in the measurements.

So, it seems to me, that the fact of variations, in some cases rather large, does not in the least show that these polarizable cells have no definite electromotive force, when the difficulties of measurement are taken into account; and further until recently all the measurements have been made with a galvanometer, which is ill suited for polarizable cells.

We will consider again Nernst's formula for the reversible cells,

$$\pi = \frac{RT}{ne}\left(\log\frac{P_1}{P_2} + \log\frac{p_2}{p_1}\right) \times 10^{-4}\ volts,$$

and the particular case where $p_2 = p_1$

$$\pi = \frac{RT}{ne}\left(\log\frac{P_1}{P_2}\right) \times 10^{-4}\ volts,$$

and see how well it predicts the facts for the polarizable cells we have been considering. We have found the cells to be independent of the concentration, as the formula would indicate. Ostwald[1] and LeBlanc[2] state definitely that *log* P_1 the solution pressure of the electrode metal, depends solely upon the metal and the temperature, and is independent of the negative ion of the solution. This being the case we would expect the electromotive force to depend solely on

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[1] Lehrbuch, 2d Ed. 2, 855.

[2] Elektrochemie, 184.

the electrode metals and to be independent of the salt in which they are immersed; and this Bancroft found to be true when mercury was not used as an electrode. The figures given by him in the first part of Table V are a striking confirmation of this fact. But when we consider the cells in which mercury or copper serve as one of the electrodes, then this is not true in the least, and the negative ion of the salt solution seems to have a very definite effect, for in the cells Zn | Hg and Cd | Hg there is always observed an increase of electromotive force of 0.3 volts in passing from the iodide to the chloride cell, and about 0.16 volts in passing from the iodide to the bromide. These values seem to be perfectly well defined, and are surely not due to experimental error.

Let us now further consider the value of the solutiion pressure and inquire into the single potential difference between a metal and a solution. The assumption of Nernst is that, when a metal is immersed in a solution of a salt of the metal, if the solution pressure of the metal be greater than the osmotic pressure of the metal ions in the solution, then positive metal ions will go from the electrode into the solution and the electrode thus become negatively charged to the solution. If, however, the osmotic pressure of the ions in the solution is greater than the solution pressure, then metal ions will be precipitated from the solution on the metal, thus charging the electrode positively to the solution. What happens when we consider cadmium and mercury in salts of the alkali metals and the single potential differences arising therefrom? The solution pressure of cadmium is large and we would expect the cadmium to be charged negatively to the solution, and this is actually found to be the case when the single potential differences are measured by the method of the dropping mercury electrodes. But with mercury or copper the metal is found to be positive to the solution. How does this come about? There are no mercury ions in potassium sulphate to be precipitated on the mercury. Yet we may assume with Warburg that oxygen contained in the electrolyte dissolves up some mercury. Then we can say that the mercury ions are precipitated on the mercury again, if their osmotic pressure has become greater than the solution pressure of the mercury. It does not, however, seem entirely correct to assume that mercury goes into solution only to be again precipitated, and by this precipitation the mercury become positively charged. The following equations express the reaction,

$$2\ Hg + O + H_2O = HgO_2H_2 \rightleftarrows 2\ \overset{++}{Hg} + 2\ \bar{O}_2\bar{H},\ \text{or}\ O + H_2O = 2\ \overset{-}{OH},$$

or in other words, in the presence of mercury, oxygen unites with water to form two hydroxyl ions.

However this may be, the single potential differences measured by the dropping mercury electrodes do make cadmium negative and mercury positive to solutions of potassium salts just as to salts of the electrode metals. It is also interesting to see if the single potential differences vary with the nature of the negative ion in any or all cases. If the assumption of Ostwald with regard to the solution pressure be true, then there would be no variation. The method of dropping mercury electrodes does not give very accurate results, but it is sufficiently accurate to point out the facts desired. The values $M_1|RX$ and $RX|M_2$ do give when added the value for the cell $M_1|RX|M_2$. Values found for Zn, Cd and Hg by Paschen[1] and for Cu by Ostwald[2] are given in Table VI.

Ostwald made measurements on a large number of metals and acids and came to the conclusion that the halogen acids differ from the oxygen acids, the latter forming a group by themselves. With the more dilute acids this is very noticable. Zn|Hg shows with most oxygen acids a value of approximately 1.4 volts, hydrochloric acid 1.2 volts, hydrobromic acid 1.0 volt and hydriodic acid 0.8 volts. In most cases the numbers with increasing dilution tend toward the negative side. Whether the influence of dilution is great or small depends upon the metal and upon the acid. Zn, Fe and Bi show the greatest changes, while Cd, Pb, Cu, Ag and Hg show comparatively little change. In all cases dilution has no great effect with the organic acids.

Paschen made measurements between metals and salt solutions not containing the electrode metal as ion. His conclusion is that the potential difference depends upon the anion and not on the cation

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[1] Wied. Ann. 43, 590 (1891).

[2] Zeit. phys. Chem. 1, 601 (1887).

TABLE VI.

Solution	Zn|Sol.	Cd|Sol.	Sol.|Hg	Sol.|Cu	Solution	Zn|Sol.	Cd|Sol.	Sol.|Hg	Sol.|Cu
HCl = 1 l.	0.560	0.248	0.560	0.305	HBr = 0.272 l.	0.393	0.175	0.503	
= 10 l.	0.610	0.272	0.551	0.367	= 0.9833 l.	0.423	0.202	0.490	0.316
= 100 l.	0.643	0.242	0.548	0.414	= 10 l.	0.567	0.238	0.493	0.394
KCl = 0.280 l.	0.525	0 260	0.524		= 100 l.	0.610	0.246	0.496	0.410
= 1 l.	0.547	0.249	0.539		KBr = 0.402 l.	0.399	0.203	0.474	
= 10 l.	0.575	0.251	0.553		= 1 l.	0.441	0.186	0.483	
= 100 l.	0.523	0.240	0.584		= 10 l.	0.422	0.167	0.493	
NaCl = 0.239 l.	0.521	0.262	0.562		= 100 l.	0.496	0.183	0.505	
= 1 l.	0.512	0.266	0.556		HI = 10 l.	0.427	0.117	0.411	0.320
= 10 l.	0.541	0.268	0.557		= 100 l.	0.515	0.159	0.417	0.301
= 100 l.	0.557	0.268	0.590		= 1000 l.	0.584	0.214	0.386	
$MgCl_2$ = 0.971 l.	0.525	0.252	0.546		KI = 0.795 l.	0.250	0.113	0.400	
= 2 l.	0.531	0.277	0.547		= 1 l.	0.233	0.113	0.400	
= 20 l.	0.598	0.258	0.548		= 10 l.	0.308	0.110	0.412	
= 200 l.	0.516	0.245	0.580		= 100 l.	0.369	0.120	0.412	
$BaCl_2$ = 0.809 l.	0.512	0.259	0.562		= 1000 l.	0.454	0.199	0.386	
= 2 l.	0.554	0.249	0.555		K_2SO_4 = 2.152 l.	0.618	0.287	0.700	
= 20 l.	0.583	0.281	0.553		= 20 l.	0.573	0.274	0 720	
= 200 l.	0.566	0.240	0.586		= 200 l.	0.592	0.252	0.730	
H_2SO_4 = 2 l.	0.653	0.319	0.835		H_2SO_4 = 1 l.				0.408
= 20 l.	0.668	0.284	0.817		= 10 l.				0.369
= 200 l.	0.668	0.261	0.825		= 100 l.				0.364

in the solution.[1] Especially with like concentrations of salts having the same anion, are the same values obtained. From these measurements of Ostwald and Paschen it is rather difficult to determine whether the potential difference varies with the concentration of the electrolyte or not. The variations are not at all large except in certain cases, and may in general come within the limits of experimental error. Further, if we consider the two cells $Cd|KCl|Hg$ and $Cu/KCl/Hg$ which were found to be invariable over a very wide range of concentration, we may come to one of two conclusions with regard to the single potential differences. Either they do not vary at all with the concentration, or the variation is equal in each case and consequently does not appear in the electromotive force. Bancroft adopted the first view, but later work on my part seems to point to the latter alternative as the more probable of the two.

Further, what do the single potential differences show with regard to the effect of the negative ion? Does the negative ion have an effect simply on mercury and copper, as the measurements on the cells might indicate? From the measurements of Paschen, Bancroft saw that with Cd, Hg and Zn the negative ion always had an effect. Further in passing from the chloride to the iodide a difference of about 0.15 volts, and from the bromide to the iodide a difference of 0.08 volts was to be observed. Now in measuring the $Zn|Hg$ or $Cd|Hg$ cells a difference of 0.3 volts was noticed between the chloride and iodide cells, and 0.16 volts between the chloride and bromide cells, while $Zn|Cd$ was the same for chlorides, bromides and iodides. This showed that the effect of the negative ion was the same on all the metals considered, but that with mercury the sign was different. The numbers assigned by Bancroft as being the most probable values for Zn, Cd and Hg in chlorides bromides and iodides are given in Table VII. In addition to these values, I have calculated from my measurements the values for the sulphates and for copper in chlorides and sulphates, in the following manner:

$Cd|K_2SO_4|Hg = 1.035$
$Cd|K_2Cl|Hg = 0.815$
$2(SO_4 - Cl) = 0.220$
$SO_4 - Cl = 0.110$

$Cd|K_2SO_4|Cu = 0.728$
$Cd|K_2SO_4 = 0.365$
$SO_4|Cu = 0.363$

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[1] Wied. Ann. **43**, 570, 608 (1891).

Cu | KCl | Hg = 0.252
Cl | Hg = 0.562
Cu | Cl = 0.310

TABLE VII.

Solution	Zn | Sol.	Cd | Sol.	Sol. Hg	Sol. | Cu
Chloride	0.589	0.255	0.562	0.310
Sulphate	0.699	0.365	0.672	0.363
Bromide	0.507	0.174	0.483	
Iodide	0.436	0.104	0.410	

It will be seen that with copper the value due to the negative ion is not the same in value as with Zn, Cd and Hg. It has, however, the same sign as the term for mercury, but a smaller value. In passing from a chloride to a sulphate, with copper there is a difference of but 0.053 volts instead of 0.110 volts, so that when combined with Zn, Cd or Hg the electromotive force always appears to be a function of the negative ion.

The following table will give the values obtained for the single-liquid reversible cells, Zn | Hg, Cd | Hg, Zn | Cd, Zn | Cu, Cd | Cu and Cu | Hg, from actual observation and by calculation from Table VII. The first three series of cells were measured by Bancroft, the last three by myself, as were also the sulphates.

TABLE VIII.

Solution	Zn | Hg		Cd | Hg		Zn | Cd	
	calc.	obs.	calc.	obs.	calc.	obs.
Chloride	1.151	1.151	0.817	0.817 0.815	0.334	0.333
Sulphate	1.371		1.037	1.035	0.334	0.334
Iodide	0.846	0.847	0.514	0.515	0.332	0.331
Bromide	0.990	0.991	0.657	0.659	0.333	0.333

Solution	Zn | Cu		Cd | Cu		Cu | Hg	
	calc.	obs.	calc.	obs.	calc.	obs.
Chloride	0.899	0.897	0.565	0.565	0.252	0.252
Sulphate	1.062	1.061	0.728	0.728	0.309	0.306

It is an easy matter to give a formula for these cells if we consider the single potential differences made up of two terms; one due to the metal and the solvent, and the other due to the negative ion. Now we have found that in all cases except with copper the term due to the negative ion is independent of the metal considered. So, for the potential differences Zn | K_2SO_4, Zn | KCl, Cd | K_2So_4, Cd | KCl, Hg | K_2SO_4, Hg | KCl, Cu | K_2SO_4, Cu | KCl, we may write $A+a$, $A+b$, $B+a$, $B+b$, $C-a$, $C-b$, $D-a_{,}$ and $D-b_{,}$. We would then have for the cells Zn | K_2SO_4 | Cd and Zn | KCl | Cd the formulæ $A+a-B-a$ or $A-B$, and $A+b-B-b$ or $A-B$ for the electromotive forces; that is, the values of the two cells are equal and independent of the negative ion. For the cells Cd | K_2SO_4 | Hg and Cd | KCl | Hg we should have $B+a-C+a$ or $B-C+2a$, and $B+b-c+b$ or $B-C+2b$. The two values are not equal and a term due to the negative ion comes in, which is twice the value of the term due to the negative ion in the single potential differences. Similarly we should have for Cu | K_2SO_4 | Hg and Cu | KCl | Hg, $D-a_{,}-C+a$ or $D-C+a-a_{,}$ and $D-b_{,}-C+b$ or $D-C+b-b_{,}$.

In view of the measurements of Bancroft on Sn, Pb, Bi and Mg combined with Cd or Zn in chlorides, bromides, iodides, sulphates, nitrates, acetates, carbonates and oxalates, in which he found that the electromotive force is a function of the electrode metals and independent of the negative ions, we may conclude that with all of these metals the term due to the negative ion has the same numerical value and the same sign, and consequently disappears when the metals are combined in a one liquid cell. With mercury the values for the various negative ions are the same as with the metals just enumerated but having opposite sign. With copper the term due to the negative ion has the same sign as with mercury, but has a smaller numerical value than the corresponding term with mercury. With platinum the term due to the negative ion has not the same value; and further cells, in which platinum serves as an electrode, vary with the concentration.

Very little work has been done on the measurement of single potential differences with reversible electrodes. Le Blanc[1] made a

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[1] Zeit. phys. Chem. **12**, 345 (1893).

few measurements by determining the decomposition point of certain normal salt solutions. Neumann[1] has made quite a list of measurements on the potential difference between a metal and normal solutions of sulphates, chlorides, acetates and nitrates of these metals. These measurements were made with the aid of a normal mercury-calomel electrode, consisting of mercury in a normal potassium chloride solution to which an excess of calomel was added. Ostwald gives the value 0.560 volts to this normal electrode, and its value has been found to be extremely constant by Coggeshall.[2] The method of determining the single potential differences was by measuring the electromotive force of a cell composed of the calomel electrode combined with the metal and electrolyte whose potential difference was desired, and subtracting the value 0.560 volts from this. From these single potential differences may be obtained by addition the values for the electromotive force of reversible cells; and the values thus obtained for reversible cells agree very well with the values directly measnred. Now let us further consider the single potential differences involved in one or two concrete examples of a cell composed of two metals and two electrolytes *e. g.* $Zn|Zn\,SO_4|Hg_2\,Cl_2KCl|Hg$, $Cu|CuSO_4|Hg_2Cl_2KCl|Hg$ and $Zn|ZnSO_4|CuSO_4|Cu$. We then have in the first case the four potential difference :

A between Zn and the electrolyte $ZnSO_4$.
B between $ZnSO_4$ and KCl.
C between KCl and Hg.
D between Zn and Hg.

This last value D is negligible. The value of the cell is then $A+B+C$, similarly for the second cell we have $A_1+B_1+C_1$ and for the third $A+B_2-A_1$. By subtracting the second from the the first value $A-A_1+(B-B_1)$ is obtained, and this was found experimentally to agree with the formula $A+B_2-A_1$. The assumption is made from the formulæ given by Planck and Nernst that the values B, B_1 and B_2 are very small, but I do not know that there are any measurements that make this entirely justifiable. It is easily seen that the only assumption which need be made, that the sum of the first

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[1] Ibid. **14**, 225 (1894).
[2] Zeit. phys. Chem. **17**, 62 (1895).

two cells shall give the third, is that $B_2=B-B_1$. Now if B_2 is small or zero then B and B_1 may have any values provided that they are equal or nearly so. If, however, the values B and B_1 are not so small as to be neglected, the single potential differences of Neumann are incorrect by just such an amount.

The following values are given by Neumann as the absolute potential of the metals in their normal salt solutions.

TABLE IX.

Metal	Sulphate	Chloride	Metal	Sulphate	Chloride
Mg	1.239	1.231	Bi	—0.490	—0.315
Al	1.040	1.015	As		—0.550
Mn	0.815	0.824	Sb		—0.376
Zn	0.524	0.503	Sn		—0.085
Cd	0.162	0.174	Cu	—0.585	
Tl	0.114	0.151	Hg	—0.980	
Fe	0.093	0.087	Ag	—0.974	
Co	—0.019	—0.015	Pd		—1.066
Ni	—0.022	—0.020	Pt		—1.140
Pb		—0.095	Au		—1.356

It will be seen that the sulphates and chlorides do not vary much. As the solutions are all normal, Neumann explains the differences by the fact that the dissociation cannot be assumed to be complete, and consequently the osmotic pressures of the cation can not be assumed to be equal. To prove that on sufficient dilution the apparent effect of the anion will disappear completely, he measured thallium in solutions of tenth, fiftieth and hundredth normal thallium salts. With the hundredth normal solutions the same value within a millivolt was obtained in every case, and further a very satisfactory increase of potential with dilution. The measurements are not as convincing as they might be if the various halogen acids had been used, in which in other cases the largest effect due to the negative ion has been observed. He did measure hydrochloric and hydrofluoric acid salts, but the remaining salts are salts of organic acids; and Ostwald previously found that all the organic acids gave about the same value, and that very near to sulphuric acid. What influence the fluorine ion may have in other cases I do not know, as I think no other measurements have been made with it.

I made a few measurements on one-liquid cells reversible with respect to one of the electrodes,

TABLE X.

Electrodes	Electrolyte	Concentration	E. M. F.
$Cd \mid Hg$	$CdCl_2$	n / 20	0.814
$Cd \mid Hg$	KCl	n / 20	0.815
$Cd \mid Hg$	$CdSO_4$	n / 10	1.041
$Cd \mid Hg$	K_2SO_4	n / 20	1.034
$Cu \mid Hg$	$CuSO_4$	n / 20	0.309
$Cu \mid Hg$	$CuSO_4$	n / 10	0.303
$Cu \mid Hg$	H_2SO_4	n / 20	0.353
$Cu \mid Hg$	K_2SO_4	n / 20	0.306
$Cd \mid Cu$	$CdCl_2$	n / 20	0.565
$Cd \mid Cu$	KCl	n / 20	0.565

and found that in every case they agreed very nearly with the values obtained from the cells in which potassium salts served as electrolytes. The most natural conclusion to draw is that the single potential differences are the same in corresponding cells, that is, $Cd \mid CdCl_2$ is the same as $Cd \mid KCl$ etc. We are practically forced to this if we consider the potential difference at the cathode independent of the concentration or to be practically independent of the nature of the cation, when this is not the same as the electrode metal, as the measurements of Paschen would indicate. However, the values which would thus be obtained for single potential differences at reversible electrodes do not at all agree with those obtained by Neumann, especially in the case of copper. My values for copper are about the same as those obtained by Ostwald for the free acid.

[*To be continued.*]

CHEMISTRY AND ITS LAWS.[1]

BY F. WALD.

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1. Upon the invitation of Mr. Trevor I communicate in the following a *résumé* of my views and more recent results.

In order to appreciate properly the peculiar position occupied by chemistry in the study of the formation of mixtures, it is first necessary to recall the more general propositions concerning the equilibrium of miscible substances, propositions which we owe to J. W. Gibbs.[2]

The different homogeneous bodies which can be produced from a group of n components, and whose form and quantity do not necessarily enter into consideration, are designated by Gibbs as *phases*. Phases which can exist together separated by plane surfaces, and whose equilibrium is not dependent upon passive resistences,[3] are termed *coexistent*. The n components of a phase are independently variable when the phase of $n+1$ independent variations. A system of r coexistent phases having as a whole n independently variable components is capable, according to the Gibbs phase rule, of $n+2-r$ independent variations.[4]

Respecting the quantities whose variations can be considered together, the studies of Gibbs yield in his equations (99) to (103)[5] a varied choice ; the consideration of the quantities t, p, μ_1, $\mu_2 \cdots \mu_n$ being the best for most purposes. We have now to concern ourselves with specifically chemical questions, so for this reason it will be well to make the selection in a manner best corresponding to the

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[1] Translated, from the author's German manuscript, by J. E. Trevor.

[2] J. W. Gibbs. On the Equilibrium of Heterogeneous Substances. Transactions of the Connecticut Academy. Vol. 3.

[3] *l. c.* pages 110-112 of the English Edition.

[4] *l. c.* pages 152-153.

[5] *l. c.* page 143.

methods of chemical operations. The chemist operates usually with independently variable temperature t, variable pressure p and variable proportions[1] of the n components. Equation (102) exhibits the relation in which these quantities stand to the function ζ, a function which, however, shall not be considered here. The phase rule presupposes that the number of independently variable components is known, while frequently in chemical practice (and always at the outset of the study of yet uninvestigated bodies) a knowledge of these must first be sought. In order to take account of this circumstance, as well as for other reasons, it will be convenient to have a peculiar name for the N substances of which the system of phases is made up and which are not necessarily identical with the n components. They shall be termed *system-components*,[2] to denote that possibly the phases can not be prepared *singly* from them because the actual components may occur in the system-components in such distribution that, for the formation of a given phase from the system-components, the transfer of certain quantities of these latter to an adjoining phase would be necessary. This will be the case, for example, when a phase contains less of a component than does either of the system-components.

We shall consider first, however, a case in which the system-components can be regarded as at the same time components of the phases (and accordingly $N=n$) ; but we wish to emphasize that systems of phases are also possible in which the several proportions of the system-components can have *dependently variable* values, although one considers usually only systems of phases in which the dependence of certain variations of the masses, as demanded by the phase rule, is compatible with the constancy or even possible arbitrary variation of these proportions,—this dependence applying then only to the potentials μ of the components[3].

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[1] *Mischungsverhältnisse.*

[2] For Wald's System-components the translator would suggest the term *Constituents*,—which has been employed during the past two years in his lectures on mathematical chemistry, in making this distinction between constituents and components.

[3] If the proportions, by weight, of dependent components are arbitrarily variable, the corresponding number of components, in unaltered state, obviously must be at the same time *phases* of the system ;—their quantity is of course immaterial.

The $n-1$ independent proportions of the components receive *dependently variable* values when the components are *miscible* in all proportions. We shall presuppose accordingly that the system-components can form a homogeneous phase at any temperature, under any pressure and in any proportions. Suitable examples can be found in homologous series of organic substances, as for example the alcohols, or mixtures of alcohols which are employed in the formation of new mixtures.

In order to characterize our $N-n$ system-components as at the same time components in general, we further assume them to differ in such wise that no one of them can be produced through combination of the others into a single phase—while in all other respects their chemical character can remain entirely unknown—and we assume also that every phase in the system can be produced *singly* from the system-components.

In the employment of system-components with so unlimited miscibility, every variation in their relative proportions will obviously result in the disappearance of a phase unless it be compensated by $r-1$ variations, as the phase theory indeed *in general* demands. If r phases are given and (for $r \leqq n$) p and t are independent, every independent variation will necessitate the changing of $r-1$ proportions to new values. But this would require very unusual and exceedingly difficult operations, allied to «titration», which would have to be undertaken simultaneously with r substances in order merely to ensure the existence of the phases.

It may be noted in passing that in the interval which would be required for the execution of these operations, the coexistence of r phases could not subsist; and that then all r phases necessarily would have dependently variable composition.

2. Although cases of the presupposed kind can doubtless be realized, there exists probably (because of the enormous experimental difficulties) no single example of an investigation relating to the conditions of coexistence of phases so essentially instable. All actually executed investigations concern cases in which the proportions of the system-components are either entirely arbitrary, or at least may remain constant[1]; the miscibility of natural substances is

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[1] Independent variations of the several proportions do not necessarily correspond to independent variations of the system of phases; see last foot-note.

accordingly often far less than we have assumed, or than might generally be the case so far as the phase theory is concerned.

An attempt to follow up the causes of this more limited miscibility of the majority of accessible substances would probably not be worth while; possibly these substances behave differently upon other heavenly bodies or at higher temperatures. In any case, we human beings, our bodies being complicated complexes of phases, could not exist under such conditions.

This limited miscibility manifests itself in gradually differing ways. Often merely the dependent variations of the several proportions disappear, and the circumstance that the corresponding system-components may be united to a homogeneous phase only in certain limited (though still variable) proportions, is very probably related closely therewith. In other cases the phases no longer can be produced singly from the system-components, but only simultaneously in greater number, so that the system-components themselves must be regarded as made up of yet other substances. The miscibility can be even so far restricted that at times impassible limiting values are set to the proportions in which the components can appear.

The number n of the components is therefore not always identical with the number N of the system-components; it must be determined empirically.

3. Not all degrees of limited miscibility arouse equal interest in the investigator; the frequent compatibility of constant or even arbitrarily chosen relative proportions of the system-components with the coexistence of phases during other variations, is so common a phenomenon that it is regarded as almost self-evident. The circumstance too that not all substances can be united in all proportions to a homogeneous phase seems even less striking. On the other hand, it must attract attention that frequently phases are obtained which can not be produced *singly* from the system-components, for such phases have often been entirely unknown bodies. These cases are the ones which chemistry has selected as the *first* objects of its study.

An exact discussion of the thermodynamic conditions under which the phenomena of limited miscibility can appear may lead very probably to the conclusion that these phenomena are closely related to the existence of *limiting mixtures*, whose content in the single components can not, at least in one direction, be exceeded. Be that as it may, it has been determined by Proust that such mixtures exist, and ever since that time chemistry has made their study its *second* task.

The chemical study of the natural substances falls accordingly into two distinct stages:—in the first, one seeks the number of independent components of the given system-components and of the phases formed from them, or, in other words, the least number of substances requisite for the separate preparation of each of the system-components as well as of each of the phases which are produced; in the second stage, those phases are sought whose material character remains uninfluenced by the independent variations of the systems of phases in which they arise.

Chemistry, according to this exposition, is concerned solely with the more striking effects of limited miscibility, and therefore with an arbitrary (although very suitable) *selection* of phases and of systems of phases; and it has determined a series of peculiar laws which apply to them. To account for these laws, it has been deemed necessary hitherto to accept certain hypotheses. My view, on the contrary, is that these laws are simply consequences of the conditions under which the substances in question have arisen and through which they are distinguished from phases in general. The stoichiometric laws hold, not for all phases whatever, but only for very definitely characterized ones; there apply accordingly to the latter not only all laws to which phases in general are subjected, but also *in addition* certain special relations which must hold good if the phases in question are to satisfy the requirements through which their exceptional position as *chemical* phases is obtained.

4. In the analytical stage of chemical investigations, which must be imagined as beginning in a time when no chemical knowledge whatever had been attained, N substances are mixed in variable proportions by weight, at variable temperature and under any (usually accidental) pressure, and the number of phases which can exist under the given circumstances is determined. If none of the N substances can be obtained as single phases by mixing the others, it follows that each must contain at least one component peculiar to itself. Now it is to be expected that the mixture will be one homogeneous phase; if the experiment yields more than one, each differing from the system-components, we must assume $r-1$ further components,—and from this it must be concluded that at least $n \geq N+r-1$ components are present. When single phases turn out to be identical with certain system-components they are not counted; if it appear on the other hand that apparently identical system-components, according to their origin or other circumstances, do give differing systems of phases under otherwise like conditions, then so many more components must be counted as dependent variations of this kind are observed.

These methods of reasoning are still employed in the chemical investigation of unknown substances; they embody an empirical form of the phase rule,—they yield the number of independent components from the observed number of phases and the number of the independent variations consistent with the existence of these phases. If one is convinced that these last data have been correctly determined, he feels equally certain about the number of independently variable components, and sets, with the above mentioned possible corrections,

$$n=N+r-1.$$

That one can be deceived in this, however, appears from the fact that independently variable components are often discovered even in very thoroughly investigated substances, be it for the reason that single phases have been overlooked because of their small quantity or of their similarity with others, or that the observed number of independent variations is too small. It may also transpire that entirely unsuspected components of these substances can be discovered upon mixing the latter with other bodies.

If the new components thus found render possible ***independent*** variations of the system of phases, they of course require an increase in the number n formerly accepted as correct. Otherwise these components can be ignored so long as one is concerned with but a single definite system of phases. But if it be desired to consider simultaneously a number of such systems, it may become necessary to employ the elaborated phase-formula $n-h+2-r$ of Gibbs, where h denotes the number of components whose quantity in the system of phases stands in an invariable ratio by weight to the quantity of others.

5. Chemical sytematics is concerned with substances, the number of whose components usually may be regarded as known, and which suffer no change of composition as a result of any dependent variations of the system to which they as phases belong.

In order that a substance may be termed a *chemical individual*: *a.* It must arise from a group of phases in which the several proportions of all the system-components are independently variable, whereby, however, as has been noted often already, the potentials μ of certain components (or possibly of all) may yet be dependent; *b.* The system of phases must admit at least *one* independent variation, from which follows that it can contain at most $r=n+1$, or $r=n-h+1$, phases respectively ; *c.* And finally, during all variations, its character (but not its quantity) must remain appreciably the same as though it, as individual phase, were enclosed in a shell impermeable for every substance.

This latter condition is identical with the requirement of constant composition, but the form of statement here adopted has the advantage of making clear that a substance may be declared a chemical individual before any idea has been formed regarding either its components or the relative proportions in which these components appear.

Accordingly, when we speak of a chemical individual, the question remains entirely open whether the substance is actually undecomposable, or whether we do not yet know how to effect a decomposition of it.

It has not yet been found possible to free from independently variable components certain bodies which are regarded as chemical individuals, but on the assumption that, nevertheless, it is possible to do this, the phase in question is treated as an unchemical mixture of the yet unknown chemical individual with these components.

To term the composition of a phase *chemically* constant is intended to signify briefly that the above enumerated conditions are fulfilled.

If substances which are completely miscible within certain limits are mixed always in the same (although arbitrary) proportions by weight, a product of invariable composition is of course always obtained; but this kind of constancy is, according to the above definition, not at all a chemical one. If, therefore, it should happen that one component of a body is known to be producible from other components, and it is desired to employ these latter, it must be permissible either to employ these components themselves in independent relations by weight, or else[1] to introduce the complex component, as formed from them, into the system in the form of a chemical compound. In the latter case then the criteria of chemical individuality must be applicable in the first place to the system-component in question. Similarly, when we are called upon to apply the phase rule in the form $n-h+2-r$, the phases of constant composition which are obtained may be regarded as chemical individuals only when every one of the components included under h is employed in a chemical compound.

Substances already recognized as chemical individuals can be prepared of course in any other manner suited to the purpose in hand; but for each of these bodies methods of preparation must exist through which it is proved to be a chemical individual,—and it is precisely these methods which alone have interest for us. It is to be noted that in the systems produced by these methods, the variations which may be regarded as independent can be no longer chosen arbitrarily. Of the physical parameters p and t, one at least must be independent, and if the system admits two variations it must be possible to vary both p and t independently. If yet other variations are permissible, then, together with p and t all the components which may be present only in chemical union with others in the system-components are dependently variable, and of the system-components themselves all those which at the same time form phases of the system.

6. The aim of chemistry is to resolve all mixtures into chemical individuals, and this result has been reached in surprisingly many cases. We may be justified in assuming, therefore, that all our system-components are chemical individuals, and that the phases formed from them are either themselves chemical individuals or can

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[1] If this procedure should be incompatible with the subsistence or constant composition of the phase.

be resolved into such. If a system contain phases of variable composition we may imagine these separated into chemical individuals by «semipermeable walls», whereby one phase with dependently variable osmotic pressure is obtained for every independently variable relative proportion of the system-components. Phases whose quantity can neither be increased nor diminished by chemical reactions among the other phases may be ignored entirely, since we omit them from the number of the n components. But if further phases then remain with dependently variable composition—as, for example, in dissociating water vapor, from which oxygen and hydrogen can be separated, but pure water can not—we can disregard this system of phases altogether. For if its chemical components are all known they must have been recognized as chemical individuals from other systems in which no phases with dependent composition appear.

In the systems which need be considered all phases are accordingly chemical individuals, and all system-components are at the same time phases; the chemical reactions occurring in these systems must therefore be thermodynamically reversible. In the place of a pressure common to all phases we have possibly a number of osmotic tensions, yet, regardless of this, we may speak of *one* pressure p which is either common to several phases or concerns but a single—arbitrarily chosen—one.

The number of phases can not be greater than $n+1$ (or $n-h+1$ respectively), and not less than n (or $n-h$). No further limitation is imposed upon the character of the phases than that they must be chemical individuals; but in no wise can anything be stated as to whether one or another contains one component or several. It must be admitted, therefore, on the other hand, that every known compound of several components can belong to a system of phases of the kind here presupposed, in which moreover all of the phases—whether initial or subsequently produced—necessary for the reaction are *compounds* of the n, or of the $n-h$, components.

The correctness of this proposition becomes more clear when its contrary is assumed as correct: that every reaction of chemical compounds involves a co-operation of the free components. Now, for us, only the so-called elements are undecomposable, and indeed these may not be so to-morrow; but, apart from this, $n-1$ elementary components would then have to form phases in every system having $n-h$ independent components. We should be forced to conclude that even when h becomes zero two chemical compounds at most of the same substances could be capable of existence under independent temperature and dependent pressure. In chemical analysis, where the pressure is independently variable also, only *one* chemical compound could exist, and no compound could contain dependent (h—) components. But these propositions are obviously incorrect, both in themselves and because we have no guarantee that the so-called elements are incapable of further decomposition.

But in order that every compound can be made only from other compounds, there must exist certain relations among the compositions of all, relations which are readily seen to be identical with the familiar laws of simple and of multiple proportions.

If it had ever been noticed that chemistry begins its operations with substances about whose components (either as to their number or their properties) nothing whatever is known, the existence of the stoichiometric laws never could have appeared especially striking. But it seemed more suitable to imagine all chemical compounds as individual phases arising from supposedly undecomposable components; and in consequence of this all the relations were forgotten which are necessarily bound up with the far more frequent production of these compounds from others.

7. If a system have $r=n+1$ phases the pressure is independent,—as well as the osmotic tensions eventually to be considered. But the system-components are transformable into the remaining phases and the reverse, and, further, the absolute quantity of each phase is immaterial; the pressure therefore indeed will be constant at constant temperature, but the volume of the system undergoing reaction will vary.

When only $r=n$ phases are necessary for a reaction the pressure is still independent, and if we disregard the necessity of osmotic walls there remains no further means of bringing about the reaction. (The reaction is of course supposed possible.) It follows therefore that the reaction here is thermodynamically an entirely unimportant matter, and that it can entail neither change of volume nor development'[1] of heat. For if, for example, a change of pressure produces no reaction the reaction cannot, on the other hand, effect a change in the volume. If osmotic walls are necessary for the separation of the system into chemical individuals, then this conclusion obviously must be modified in such wise that the sum of the quantities of work concerned in the reaction must disappear. Reactions in which the number of the interacting substances is equal to the number n (or $n=h$ respectively) of the components can be realized accordingly, with ordinary chemical means, only when either the substances themselves form mixtures of variable composition, or when bodies are present which, although not directly participating in the reactions, yet render possible the formation of such mixtures. It follows, from the thermal indifference of these reactions, that the sum of the specific heats of the products of the reaction must be equal to the sum of the specific heats of the system-components ;—but the necessity of osmotic walls for the separation of substances into chemical individuals may introduce apparent exceptions. In any case the bodies must all be considered in the state in which they participate in the reaction ; for example, that the specific heat of carbon will not follow certain rules, is related very probably to the circumstance that there are few reactions if any which supply pure carbon reversibly and at the same time satisfy the condition $r=n$.

If now it can be proved that by combinations of reactions when $r=n+1$ a total reaction with $r=n$ must arise, there will follow for the latter a volume-neutrality, or a work-neutrality respectively. In consequence of this, the quantities of work which are involved in the single reactions must stand in rational numerical ratios. But for this to be true it is merely necessary that some one of the phases be common, with $r=n+1$, to at least two of the reactions, and that the two systems shall be mechanically connected in such wise that the quantity of this phase which is produced by one of the reactions shall be consumed by the other.

The stoichiometric laws of chemical masses and volumes are referred through these considerations : *a*. To the peculiar properties of those systems of phases which have been arbitrarily chosen

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[1] Positive or negative.

as objects of chemical study, and accordingly to the fact that phenomena of this kind exist ; *b.* To the fact that «simple» components need not necessarily occur in every group of phases ; *c.* To general laws or groups of phases. My conceptions, while avoiding all hypotheses, possess the advantage of permitting conclusions to be drawn concerning a series of relations which already have been recognized in part, but have remained without explanation, and which in part have not yet been even suspected.

8. We shall busy ourselves next for a moment with reversible reactions, for which $r=n$; thermodynamically these are wholly indifferent. If we set out from a definite state of a system, subjecting the latter successively to an isothermal and to an adiabatic change of state and then returning it to the initial state by an isothermal and an adiabatic change, we obtain a Carnot's cycle, which remains unaffected so far as all essential data are concerned if yet another chemical transformation forwards and backwards should be introduced at the two stages of constant temperature. But this condition certainly can be satisfied only when for the one independent pressure of the system the Marriotte-Gay-Lussac formula $pv=RT$ holds ;—only here v denotes no longer the volume of a single phase, but the volume of a complex of phases. Since it remains open to us which of the eventual osmotic pressures we desire to regard as independent, this last equation must hold true for every one of them.

Now such reactions often involve a number of phases whose volumes are relatively very small and nearly independent of the temperature and the pressure ; these are the non-volatile substances. If their volumes are neglected, the pressure-volume law follows for the remaining phases as approximately true. It is then not necessary that the slight variations which remain should be accounted for through hypotheses they can be referred to entirely real circumstances. Even though no numerical evidence for the correctness of this view is available as yet, one may, nevertheless, not cast it aside as inadmissible or unfruitful.

9. In Gibbs's phase theory the fundamental equations of the phases are looked upon as independent of one another ; and from these equations follow both the values assumed in the individual phases by the relative proportions of the system-components, and those assumed by the phase-components themselves. Now in all chemical phenomena these quantities take particular values, which can hold good only when the fundamental equations satisfy definite conditions. Their deduction is a purely mathematical matter but we may nevertheless draw attention to the circumstance that for a long time certain relations among the properties of chemical individuals, and accordingly also among their fundamental equations, have empirically been recognized. Entire classes of chemical compounds in fact exhibit analogous chemical properties, as do acids, bases and salts for example, or alcohols, ketones and other organic bodies. Even the elements follow rules,—which find expression in the periodic system. These relations could not possibly exist if the equations of condition of the chemical individuals were as independent of one another as are those of phases in general; so they also seem to me to furnish a very trustworthy support for my views.[1]

Kladno, August 1, 1896.

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[1] In this article, on page 21, the words "is capable" are missing after the word "phase" on line 14. On page 32 also, line 4, "or" should be "of"; and on the seventh line from below a comma should appear after "hypotheses."

ON TERNARY MIXTURES.

SECOND PAPER.

BY WILDER D. BANCROFT.

In a previous paper[1] I have shown that the general formula

$$\frac{x^\alpha y^\beta}{z^{\alpha+\beta}}=constant \qquad \text{(I.)}$$

describes the equilibria when two non-miscible liquids are dissolved in a consolute liquid. This same equation must still hold good if I substitute a solid for one of the non-miscible liquids, nothing being allowed to vary except the change of condition of one of the components at the temperature of the experiment. As solids which are miscible in all proportions with a liquid are neither common nor easy to work with, I have thought it better to study the less simple case of two non-miscible substances, one a liquid and one a solid, dissolved in a liquid solvent in which the solid has a limited solubility, but with which the liquid is consolute. The only example of this for which I have been able to find data ready to my hand is for the equilibria between alcohol, a salt and water. Of course, formula (I) will not hold in its present form and it must be modified to give a limiting value for the salt when the concentration of the alcohol becomes zero. There are several ways of doing this; but in this paper I shall consider only one, a change in the origin of the co-ordinates. Let x represent the quantity of alcohol, y the quantity of salt in a constant quantity of water, the whole to be expressed in any units or combination of units that may be preferred. The general equation will then take the form:

$$(x+A)^\alpha y^\beta=C' \qquad \text{(II.)}$$

where α, β, A and C' are constants for constant temperature, α and

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[1] Physical Review 3, 21 (1895).

β depending on the nature of the components only, A and C' on these and on the units in which the components are expressed. Since the ratio of α and β is all that interests us at present, we may set it or its reciprocal equal to n as I have done in the first paper on this subject and we shall have, when $\beta / \alpha = n$, the expression:

$$(x+A)\,y^n = C. \qquad \text{(IIa.)}$$

This equation is in a form in which it can be tested. The best numerical data on the subject are those of Bodländer[1]. He determined the salt by evaporation of the solution and weighing the residue in the usual manner. The composition of the aqueous alcohol was obtained by distillation and examination of the distillate optically. This method can not be considered accurate, as it is necessary to distill off all the liquid without losing any, a thing very difficult to do. A slight error in the percentage composition of a mixture rich in alcohol makes a large absolute error when the concentration is expressed in grams of alcohol per hundred grams of water. It is not clear from the author's description how he kept the temperature constant or that it was kept rigidly constant.

In spite of the large experimental error in some of the data, I find that Bodländer's results are expressed with a very fair degree of accuracy by equation (II*a*), or rather by two equations of that form. This last fact makes it necessary to consider what the significance of two equations is. I found that two equations were usually necessary practically, always theoretically, to express the results with two non-miscible liquids and I showed that this was due to the fact that the precipitate changed as one passed from one curve to the other. Following out this analogy one would expect two curves also when one of the non-miscible substances was a solid, and that along one curve we should have the solid separating out and along the other the liquid, forming two liquid phases. This is exactly what we find for acetone with most salts and for alcohol with some salts. Carrying the analogy still further, we should expect that in the case of two non-miscible solids we should have one curve when the solution was saturated in respect to one salt, and another when

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[1] Zeit. phys. Chem. **7**, 308 (1891).

it was saturated in respect to the other, and that the intersection of the two curves would come at the concentration at which the two salts could crystallise side by side. As I shall show in this paper, this is what happens. We have identity of behavior as we change from two liquids to a liquid and a solid and then to two solids. This identity holds for alcohol with such substances as manganous sulfate, potassium carbonate, ferric chlorid, potassium hydroxide. It is very probable that it holds for all salts at suitable temperatures. This simplifies the case very much. We find experimentally that there are two curves when salt is precipitated by alcohol and we are forced to conclude that along the second curve the precipitation of the salt is secondary, as the primary reaction is the formation of a second liquid phase. Since there is no change in the nature of the precipitate, there must be a change in the nature of the liquid phase and we conclude that along the first curve we have alcohol dissolved in water, along the second water dissolved in alcohol. In other words, the difference in the behavior of alcohol with salt solutions is not that in some cases there is formation of a second liquid phase and in others not; but that in certain cases the first liquid phase can be in equilibrium with the second and in others not. For ternary mixtures we are able to answer Lothar Meyer's question:

TABLE I.

KCl at 14°.5

$(x+15)y^{2.5} = C_1$, $\log C_1 = 4.975$.

x	y calc.	y found	$\log C$.
0.0	33.1	33.0	4.973
3.26	30.6	31.3	4.999
5.93	29.0	29.4	4.991
13.4	25.7	25.8	4.983
20.7	23.4	22.9	4.953
29.3	21.5	20.2	4.911
34.7	20.5	19.8	4.936

$(x+15)y^1 = C_1$, $\log C_1 = 3.090$.

x	y calc.	y found	$\log C$.
80.5	12.9	12.6	3.080
120.0	9.1	9.4	3.104
441.4	2.7	1.9	2.945

«When does a mixture of alcohol and water change from a solution of alcohol in water to a solution of water in alcohol?» Before long I trust that we shall be able to answer the question when alcohol and water are the only components.

In Tables I-VII are the calculations of Bodländer's results. In all cases x denotes the grams of alcohol, y the grams of salt in one hundred grams of water. Under the heading «calc.» are the grams of salt required to satisfy the formula expressing the relation between x and y.

TABLE II.

KNO_3 at 17°.7

$(x+15)\,y^{1.4}=C \quad \log C=3.190.$

x	y calc.	y found	$\log C.$
0.0	27.5	27.6	3.193
10.9	18.5	18.5	3.188
33.4	11.9	11.5	3.172
69.2	8.0	7.9	3.178
89.3	6.9	7.0	3.202
137.3	5.24	5.25	3.191
248.4	3.5	3.4	3.156
499.0	2.2	1.4	2.928

TABLE III.

KNO_3 at 18°.

$(x+15)\,y^{1.4}=C \quad \log C=3.200$

x	y calc.	y found	$\log C.$
0.0	27.9	28.0	3.202
3.78	23.7	23.0	3.181
6.07	21.9	21.6	3.192
10.4	19.2	19.4	3.208
18.1	15.9	18.7	3.301
21.3	14.8	16.1	3.250
27.4	13.3	14.9	3.269
43.4	10.6	10.0	3.166

There are a few points which call for special notice. Bodländer makes sodium chloride more soluble at 11°.5 than at 13°.0, which must be due to experimental error. The formulæ used in calculating sodium nitrate solutions require that sodium nitrate should be less soluble at 16°.5 than at 13°.0, which is absurd. The formulæ are therefore wrong, but I am unable to correct them.

TABLE IV.

NaCl at 13°

$(x+10)\, y^{1.5}=C_1 \quad \log C_1=7.990.$

x	y calc.	y found	$\log C.$
0.00	35.7	35.5	7.984
15.07	29.2	29.7	8.023
21.35	27.7	27.9	7.998
27.14	26.7	26.4	7.969
37.93	25.2	24.7	7.945
	$(x+10)y^{1.7}=C_2$	$\log C_2=4.100$	
55.79	22.0	21.8	4.094
81.74	18.1	18.5	4.113
125.6[1]	14.4	15.1[1]	4.136
197.2	11.2	11.8	4.138
295.4	8.9	7.0	3.926
642.9	5.8	4.4	3.909

TABLE V.

NaCl at 11°.5

$(x+12)\, y^{1.5}=C_1 \quad \log C_1=8.090.$

x	y calc.	y found	$\log C.$
0.00	36.1	35.8	8.072
3.32	34.3	34.4	8.101
6.45	32.9	33.1	8.106
9.73	31.7	32.0	8.109
13.38	30.6	30.8	8.104
14.28	30.3	30.1	8.071
22.95	28.5	28.1	8.063

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[1] There is a mistake in Bodländer's data. Cf the density.

I have also calculated the results of Gérardin[1] and find that they can be expressed by the same general formula. His results are not very accurate, but they cover quite a range of temperature, and are therefore interesting as throwing light on the variation of the constants in the formula with the temperature. His data are very unsatisfactory in one sense because he made measurements in a more or less haphazard way, with one concentration of aqueous alcohol at one set of temperatures and with another concentration at another set of temperatures, so that the series are not comparable until reduced.

TABLE VI.

$NaNO_3$ at 16°.5

$(x+25)\,y^2=C \quad \log C=5.230.$

x	y calc.	y found	*log C.*
0.0	82.5	82.7	5.233
8.7	71.0	77.2	5.303
17.0	63.6	67.6	5.283
25.4	58.1	61.3	5.277
35.9	52.7	52.4	5.224
60.9	44.5	44.2	5.225
74.7	41.2	40.9	5.222
102.7	36.5	32.1	5.119
164.0	30.0	29.5	5.216
234.0	25.0	18.1	4.929
296.5	23.0	7.7	4.280

TABLE VII.

$NaNO_3$ at 13°.

$(x+25)\,y^2=C. \quad \log C=5.250.$

x	y calc.	y found	*log C.*
0.0	84.4	81.8	5.224
4.2	78.0	78.0	5.247
8.4	73.0	74.3	5.266
11.7	69.6	69.6	5.250
15.7	66.1	65.5	5.243
20.5	63.0	63.1	5.258
24.9	59.7	56.7	5.204

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[1] Ann. chim. phys. (4) **5**, 129 (1865).

The values given in the tables are obtained by interpolation from the experimental data. Where the change of solubility with the temperature can be represented by a straight line, as in the case of potassium chlorid and barium chlorid, interpolation is easy and the results are fairly accurate. With potassium nitrate and potassium chlorate, the chances for error are much greater. In view of these facts, it will be well to regard these tables as approximations only, which serve to draw attention to the laws describing the phenomena, but do not establish them definitely.[1] In Tables VIII–XIV are the results of Gérardin, while in Tables XV–XVI are the calculations of some of Schiff's[2] experiments. Some of his other data

TABLE VIII.

	KCl at 0°. $(x+9)y^{2.5}=C_0$ $\log C_0=4.590$			KCl at 10°. $(x+11)y^{2.5}=C_{10}$ $\log C_{10}=4.780$			KCl at 20°. $(x+12)y^{2.5}=C_{20}$ $\log C_{20}=4.920$		
% water	calc.	found	$\log C_0$	calc.	found	$\log C_{10}$	calc.	found	$\log C_{20}$
100.0	28.5	28.5	4.591	31.3	31.4	4.784	34.4	34.3	4.917
94.8	22.3	23.2	4.631	25.3	25.9	4.807	28.1	28.6	4.939
90.2	18.7	19.9	4.658	21.5	22.4	4.827	24.0	25.0	4.966
84.6	15.5	15.3	4.580	17.9	17.7	4.768	20.1	20.1	4.920
77.0	12.1	11.9	4.573	14.1	14.0	4.769	16.0	16.0	4.925
65.0	8.5	8.5	4.588	10.0	9.9	4.770	11.3	11.3	4.918

	KCl at 30°. $(x+14)y^{2.5}=C_{30}$ $\log C_{30}=5.073$			KCl at 40°. $(x+15)y^{2.5}=C_{40}$ $\log C_{40}=5.190$			KCl at 50°. $(x+16)y^{2.5}=C_{50}$ $\log C_{50}=5.300$		
% water	calc.	found	$\log C_{30}$	calc.	found	$\log C_{40}$	calc.	found	$\log C_{50}$
100.0	37.2	37.2	5.073	40.3	40.1	5.184	43.5	43.0	5.287
94.8	31.0	31.3	5.080	33.7	34.0	5.196	36.7	36.7	5.302
90.2	26.7	27.5	5.105	29.3	30.1	5.221	31.9	32.6	5.324
84.6	22.5	22.5	5.070	24.8	24.9	5.193	27.1	27.3	5.306
77.0	18.0	18.0	5.072	19.9	20.1	5.201	21.8	22.1	5.314
65.0	12.9	12.7	5.060	14.3	14.1	5.178	15.7	15.5	5.287

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[1] In the experiments with barium chlorid it is not clear why the strength of the alcohol should not change.

[2] Liebig's Annalen 118, 362 (1861).

TABLE IX.

	$KClO_3$ at 10°.			$KClO_3$ at 20°.			$KClO_3$ at 30°.		
	$(x+3)\,y^5=C_{10}$			$(x+3)\,y^5=C_{20}$			$(x+4)\,y^5=C_{30}$		
	$\log C_{10}=3.930$			$\log C_{20}=4.760$			$\log C_{30}=5.710$		
% water	calc.	found	$\log C_{10}$	calc.	found	$\log C_{20}$	calc.	found	$\log C_{30}$
100.0	4.9	4.9	3.927	7.2	7.2	4.762	10.5	10.5	5.707
94.8	3.8	4.0	4.053	5.5	6.0	4.933	8.6	8.5	5.737
90.2	3.3	3.3	3.962	4.8	4.8	4.772	7.2	7.2	5.712
84.6	2.8	2.8	3.926	4.1	4.1	4.756	5.3	6.3	5.706
77.0	2.3	2.3	3.907	3.4	3.3	4.692	5.3	5.2	5.695

	$KClO_3$ at 40°.			$KClO_3$ at 50°.		
	$(x+4)\,y^5=C_{40}$			$(x+4)\,y^5=C_{50}$		
	$\log C_{40}=6.395$			$\log C_{50}=7.110$		
% water	calc.	found	$\log C_{40}$	calc.	found	$\log C_{50}$
100.0	14.4	14.4	6.392	20.0	20.0	7.107
94.8	11.5	11.7	6.432	16.0	16.2	7.137
90.2	10.0	10.0	6.397	13.9	13.9	7.112
84.6	8.7	8.6	6.386	12.0	12.0	7.106
77.0	7.2	7.3	6.424	10.0	10.0	7.109

TABLE X.

	KNO_3 at 0°.			KNO_3 at 10°.			KNO_3 at 20°.		
	$(x+13)\,y^{1.4}=C_0$			$(x\ 15)\,y^{1.4}=C_{10}$			$(x+17)\,y^{1.4}=C_{20}$		
	$\log C_0=2.760$			$\log C_{10}=3.040$			$\log C_{20}=3.330$		
% water	calc.	found	$\log C_0$	calc.	found	$\log C_{10}$	calc.	found	$\log C_{20}$
100.0	15.0	14.8	2.752	21.4	21.2	3.034	31.6	30.6	3.311
94.8	11.1	11.5	2.785	16.3	16.7	3.054	24.5	24.2	3.322
90.2	8.8	9.0	2.772	13.2	13.2	3.043	20.2	20.7	3.348
84.6	6.8	6.8	2.761	10.3	10.3	3.040	15.9	16.3	3.345
77.0	4.9	4.8	2.753	7.4	7.5	3.045	11.6	11.2	3.308
65.0	3.1	2.9	2.727	4.8	4.5	3.006	7.5	7.5	3.333
55.0	2.0	2.0	2.764	3.1	3.1	3.036	4.9	5.0	3.342
35.0				1.2	1.5	3.197	1.9	2.5	3.493
13.0				0.18	0.25	3.233	0.29	0.34	3.421

	KNO$_3$ at 30°. $(x+19)\,y^{1.4}=C_{30}$ $\log C_{30}=3.605$			KNO$_3$ at 40°. $(x+21)\,y^{1.4}=C_{40}$ $\log C_{40}=3.860$			KNO$_3$ at 50°. $(x+23)\,y^{1.4}=C_{50}$ $\log C_{50}=4.070$		
% water	calc.	found	$\log C_{30}$	calc.	found	$\log C_{40}$	calc.	found	$\log C_{50}$
100.0	45.8	44.9	3.592	65.0	64.0	3.851	85.9	85.3	4.065
94.8	36.3	36.6	3.611	52.3	52.7	3.866	70.0	72.4	4.091
90.2	29.9	30.3	3.613	43.6	43.6	3.862	58.8	60.7	4.089
84.6	24.8	25.5	3.642	35.2	36.3	3.876	48.0	50.2	4.100
77.0	17.8	17.2	3.586	26.3	26.6	3.868	36.1	38.9	4.115
65.0	11.5	11.6	3.609	17.2	17.0	3.850	23.8	23.1	4.051
55.0	7.7	7.6	3.604	11.5	10.6	3.812	16.0	15.9	4.065
35.0	2.9	3.4	3.697	4.5	4.8	3.910	6.2	6.2	4.062
13.0	0.46	0.46	3.607	0.70	0.62	3.788	0.99	0.83	3.967

TABLE XI.

	BaCl$_2$ at 0°. $(x+15)\,y^{1}=C_0$ $\log C_0=4.150$			BaCl$_2$ at 10°. $(x+17)\,y^{1}=C_{10}$ $\log C_{10}\ 4.275$			BaCl$_2$ at 20°. $(x+18)\,y^{1}=C_{20}$ $\log C_{20}=4.370$		
% water	calc.	found	$\log C_0$	calc.	found	$\log C_{10}$	calc.	found	$\log C_{20}$
100.0	30.7	30.6	4.148	33.3	33.3	4.274	36.1	36.0	4.367
94.8	25.0	25.1	4.157	27.5	27.6	4.280	30.0	30.0	4.371
90.2	21.1	21.6	4.171	23.5	23.8	4.287	25.7	26.1	4.384
84.6	17.4	17.3	4.143	19.5	19.4	4.269	21.5	21.4	4.365
77.0	13.5	13.0	4.115	15.3	14.8	4.246	16.9	16.6	4.355

	BaCl$_2$ at 30°. $(x+19)\,y^{1}=C_{30}$ $\log C_{30}=4.455$			BaCl$_2$ at 40°. $(x+21)\,y^{1}=C_{40}$ $\log C_{40}=4.555$			BaCl$_2$ at 50°. $(x+22)\,y^{1}=C_{50}$ $\log C_{50}=4.633$		
% water	calc.	found	$\log C_{30}$	calc.	found	$\log C_{40}$	calc.	found	$\log C_{50}$
100.0	38.7	38.7	4.455	41.4	41.4	4.556	44.2	44.1	4.630
94.8	32.4	32.5	4.459	34.9	34.9	4.555	37.5	37.4	4.631
90.2	27.9	28.3	4.469	30.3	30.6	4.565	32.7	32.8	4.638
84.6	23.4	23.5	4.459	25.4	25.5	4.560	27.6	27.6	4.633
77.0	18.4	18.4	4.454	20.3	20.2	4.551	22.0	22.0	4.633

do not agree at all with the other work tabulated and I have omitted them for the present. The letters in the formulæ have the same significance as before; but in the first column I have placed the grams of water in one hundred grams of the aqueous alcohol used, and under the headings "calc." and "found" are the quantities of salt in grams which were dissolved in one hundred grams of aqueous alcohol of the strength specified.

TABLE XII.

KI at 18°.

$(x+3)\,y^{20}=C$

$\log C=43.60$

% water	calc.	found	*log C*
100.0	143.2	142.3[1]	43.54
94.8	129.2	130.5	43.71
90.2	119.7	119.4	43.58
77.0	97.5	100.1	43.81
71.0	88.9	89.9	43.70
62.0	76.2	76.9	43.69
55.0	66.5	66.4	43.57
41.0	48.3	48.2	43.57

TABLE XIII.

CH_3CO_2Na at 18°.

$(x+5)\,y^{30}=C$

$\log C=49.19.$

% water	calc.	found	*log C*
100.0	41.3	41.5[1]	49.23
94.8	38.2	38.0	49.11
90.2	35.9	35.9	49.20
77.0	29.8	29.8	49.19
71.0	27.2	27.5	49.30
62.0	23.5	23.5	49.19
55.0	20.6	20.4	49.04
41.0	15.2	14.6	48.70

TABLE XIV.

$SrCl_2$ at 18°.

$(x+50)\,y^{15}=C$

$\log C=27.52.$

% water	calc.	found	*log C*
100.0	52.6	52.4[1]	27.49
94.8	49.7	49.8	27.54
90.2	46.9	47.0	27.53
77.0	39.2	39.6	27.59
71.0	35.9	35.9	27.52
62.0	31.0	30.4	27.42
55.0	27.1	26.8	27.44
41.0	19.7	19.2	27.34

TABLE XV.

KNO_3 at 15°.

$(x+13)\,y^{1.4}=C$

$\log C=3.100$

% water	calc.	found	*log C*
100.0	26.2	25.8	3.091
90.0	15.2	15.2	3.101
80.0	9.7	9.3	3.070
70.0	6.5	5.9	3.043
60.0	4.3	4.5	3.126
50.0	2.8	2.9	3.122
40.0	1.7	1.7	3.091
20.0	0.4	0.4	3.037

[1] From Landolt & Börnstein's Tables.

The most striking thing about these results is that the value of n seems not to be a function of the temperature. On the other hand A changes slightly, increasing with rising temperature. It is not possible to say anything more definite than this about the rate of change because the values of A are not determined with sufficient accuracy. If we compare the experiments of Gérardin with those of Bodländer we find that in both cases the results can be described by formulæ having the same exponential factor; but the value of A is not the same. This discrepancy is due to experimental error.

TABLE XVI.

NaCl at 15°.
$(x+10)\,y^{4.5}=C_1$
$\log C_1=8.000$

% water	calc.	found	$\log C_1$
100.0	35.9	35.9	7.998
90.0	27.4	28.5	8.078
80.0	21.8	22.5	8.064
70.0	17.4	17.5	8.014
60.0	13.7	13.2	7.928

$(x+10)\,y^{1.1}=C_2$
$\log C_2=4.200.$

% water	calc.	found	$\log C_2$
50	9.3	9.8	4.230
40	6.0	5.9	4.191
20	1.7	1.2	3.936

TABLE XVII.

$\log C_{KCl}=9.017-\frac{1200}{T}$

Temp.	$\log C$ calc.	$\log C$ found
273°	4.621	4.590
283°	4.780	4,780
293°	4.924	4.920
303°	5.054	5.073
313°	5.188	5.190
323°	5.301	5.300

TABLE XVIII.

$\log C_{KClO_3}=29.85-\frac{7345}{T}$

Temp.	$\log C$ calc.	$\log C$ found
283°	3.910	3.930
293°	4.790	4.760
303°	5.780	5.710
313°	6.410	6.395
323°	7.100	7.110

Very little stress should be laid on the fact that the exponents are in most cases multiples of one-half. In view of our lack of knowledge in regard to the exponential term and of the inaccuracy of the experimental evidence, wherever it was possible to express the results at all satisfactorily by a value of *n* equal to some multiple of one-half, I have done so, although a better agreement might have been obtained by using a less simple fraction. It seemed desirable to see if a mathematical expression could be found for the change of *log C* with the temperature, and the most probable form in this case is that of van 't Hoff

$$\frac{\partial \log C}{\partial T} = \frac{B}{T^2}$$

Integrating this on the assumption that B is a constant we have

$$\log C = D - \frac{B}{T}.$$

In Tables XVII-XX are given the formulæ for each case and the values calculated from them for each temperature. As will be seen the agreement between the two sets of values is quite within the limits of experimental error.

I should have liked to have taken into account the papers of Antusch[1] and of Antusch and Holleman[2], but the originals are not

TABLE XIX.

$$\log C_{KNO_3} = 11.30 - \frac{2333}{T}$$

Temp.	*log C* calc.	*log C* found
273°	2.749	2.760
283°	3.058	3.040
293°	3.338	3.330
303°	3.591	3.605
313°	3.853	3.860
323°	4.072	4.070

TABLE XX.

$$\log C_{BaCl_2} = 7.270 - \frac{851}{T}$$

Temp.	*log C* calc.	*log C* found
273°	4.151	4.150
283°	4.264	4.275
293°	4.366	4.370
303°	4.458	4.455
313°	4.553	4.555
323°	4.634	4.633

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[1] Dissertation, Groningen, 1894.

[2] Recueil travaux. Pays-Bas **13**, 273 (1894).

accessible to me. One table of theirs is given by Bodländer[1] for the solubility of alanine in aqueous alcohol. The results are given in Table XXI. Here x denotes grams alcohol, y grams alanine in one hundred grams water. In the first column is the number of grams of alcohol in one hundred grams water. Under the headings "calc." and "found" are the grams of alanine in one hundred cubic centimeters of solution.

TABLE XXI.

Alanine at unknown temperature.
$(x+30)y=C_1 \quad \log C_1=2.700$
Alanine in 100 *cc.*

x	calc.	found	*log C*
0.0	14.95	14.75	2.694
4.17	12.68	12.94	2.709
8.69	10.81	11.31	2.719
13.84	9.08	9.59	2.724
19.45	7.82	7.81	2.700
25.65	6.62	6.56	2.696
34.20	5.38	5.20	2.685
42.85	4.45	4.54	2.709
$(x+30)^{1.5}y=C_1$		$\log C_1=3.640$	
42.85	4.54	4.54	3.640
50.12	3.73	3.58	3.622
61.10	2.86	2.85	3.639
73.96	2.16	2.17	3.640
89.75	1.59	1.63	3.652
109.2	1.14	1.41	3.733
166.4	0.52	0.74	3.791
278.6	0.22	0.32	3.886

It seems to me almost certain that if everything is expressed in grams the term A will be a function only of the salt and the solvent at constant temperature, and will be independent of the nature of the precipitating substance. The only data by which to test this assumption are the measurements of Bodländer[2] on the solubilities

[1] Zeit. phys. Chem. **16**, 729 (1895).
[2] Ibid, **7**, 360 (1891).

of KCl and KNO_3 and of NaCl and $NaNO_3$. Formula (II*a*) is not applicable to this case, for there are now under consideration two substances with limited solubility. If we treat this second complication as we did the first we shall have

$(x+A)^{\alpha}\ (y+B)^{\beta}=C'$ (III.) and $(x+A)\ (y+B)^{\kappa}=C$ (IIIa.)

The test of this equation can only be approximate owing to the large experimental error in Bodländer's results. In the table giving the solubilities of KCl in presence of varying quantities of KNO_3, he says that the last four solutions were saturated in respect to KNO_3. Under these circumstances we know that the compositions of the four solutions must have been the same; yet the analysis gives results for KNO_3 varying from 17.91 *g*. to 18.79 *g*., an error of about 5 per cent. From the table it would appear that less KCl will dissolve in a solution containing 7.67 *g*. KNO_3 per 100 *g*. H_2O than in one containing 10.42 *g*., which is obviously wrong. In spite of this uncertainty, it will be seen that formula (III*a*) expresses the equilibria between these four salts with fair accuracy in spite of the fact that we are dealing with very strong solutions. It will be noticed that the values of the constants A and B remain the same, regardless of which salt crystallises out, but that the exponential factor changes when the precipitate changes. We have here as before two curves, along one of which the solution is saturated in respect to one salt and along the other in respect to the second. The intersection comes, as it must, at the point where the two salts are in equilibrium with solution and vapor. In Tables XXII–XXV are my calculations of Bodländer's results.

While the constants are not identical with those used in the previous tables, the agreement is as satisfactory as could be expected under the circumstances. More accurate measurements will show a better result. For purposes of comparison I give in Table XXVI the values for the constant as determined from the data of Bodländer, Gérardin and Schiff for the precipitation of salts with alcohol, and in the last row the values found when one salt is precipitated by another.

In this discussion I have taken as the unit in which the results were to be expressed the gram. This has no effect on the regularities brought out. As I have already shown[1] the nature of the unit has no influence on the form of the mathematical equation describing the equilibria. It must be kept in mind that, if the results are to be expressed in volume concentrations, this value for

TABLE XXII.

KCl at 17°5
$x=g.\mathrm{KCl}$ $y=g.\mathrm{KNO_3}$
in 100g. H_2O.
$(x+13)^{10}(v+15)=C$
$\log C=34.500$

y	x calc.	x found	*log C*
0.0	33.35	33.45	34.516
7.67	32.40	32.09	34.435
10.42	32.19	32.23	34.505
14.92	31.77	31.73	34.496
17.91	31.58	31.32	34.457
18.41	31.57	31.39	34.464
18.79	31.56	31.50	34.479
18.58	31.56	31.75	34.546

TABLE XXIII.

$\mathrm{KNO_3}$ at 20°.5
$x=g.$ KCl $y=g.\mathrm{KNO_3}$
in 100g. H_2O.
$(x+13)(y+15)^4=C$
$\log C=7.775$

x	y calc.	y found	*log C*
0.0	31.26	31.28	7.774
5.37	27.45	27.74	7.778
8.85	25.64	25.60	7.777
14.12	23.50	23.20	7.761
17.66	22.33	22.13	7.767
23.28	20.81	20.98	7.784
26.61	20.00	20.51	7.798
30.34	19.28	20.40	7.833

TABLE XXIV.

NaCl at 15°.5
$x=g.$ NaCl $y=g.\mathrm{NaNO_3}$
in 100g. H_2O.
$(x+25)^9(y+10)=C$
$\log C=17.070$

y	x calc.	x found	*log C*
0.0	36.04	35.92	17.065
8.60	31.94	31.92	17.067
15.35	30.05	30.50	17.100
26.25	27.90	29.00	17.147
35.00	26.65	27.74	17.151
42.65	25.75	25.74	17.069
48.90	25.08	25.08	17.070
48.75	25.63	25.40	17.087

TABLE XXV.

$\mathrm{NaNO_3}$ at 15°.
$x=g.$NaCl $y=g.$ $\mathrm{NaNO_3}$
in 100g. H_2O.
$(x+25)(y+10)^{1.5}=C$
$\log C=4.370$

x	y calc.	y found	*log C*
0.0	85.72	82.38	4.347
5.29	74.33	74.86	4.374
9.58	67.10	68.60	4.381
14.75	60.32	61.50	4.380
19.95	54.71	55.43	4.377
23.12	51.95	51.72	4.367
24.60	50.68	50.20	4.365
24.95	50.40	46.06	4.354

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[1] Physical Review **3**, 116 (1895).

TABLE XXVI.

	KCl	KNO_3	$NaCl$	$NaNO_3$
Bodländer	15	15	10	25
Gérardin	12	17	—	—
Schiff	—	13	10	—
Found	15	13	10	25

alcohol, for instance, is $(x+A)/V$ and not x/V. By this method of treating the subject we have for the first time a means of determining whether hydrates exist as such in solution or, in more general terms, whether we have an addition of the solvent to the solute[1]. If this were the case we should no longer be working with a constant quantity of the common solvent and we should no longer get concordant results. There is no sign of any such disturbing influence in the case of $BaCl_2$. Bodländer thought that his experiments on NaCl required for their explanation the assumption of the existence of the hydrate $NaCl\,2H_2O$ in solution. It will be seen that this is incorrect and that sodium chloride shows no abnormal behavior. Another important result of this point of view is that we are not obliged to take into account the question of dissociation. It is immaterial whether one, either or both of the non-miscible substances are electrolytes.

The results of this paper may be summed up as follows:

1. The equilibria between two non-miscible substances in a common solvent are represented by the Mass Law formulæ.
2. It is immaterial whether the non-miscible substances are both liquid, both solid or one liquid and one solid in the pure state at the temperature in question.
3. It is immaterial whether either, one or both are electrolytes.
4. When one of the non-miscible substances is infinitely, the other partially, miscible with the common solvent, the equation describing the equilibria is of the form: $(x+A)y^n=C$.
5. The value of n is independent of the temperature over a range of 50°.

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[1] Cf. Neust. Theor. Chem. *p.* 370.

6. The value of A is not a function of the other non-miscible substance.

7. The value of A increases with increasing temperature.

8. The change of $log\ C$ with the temperature is given by the equation:

$$\frac{\partial\, log\ C}{\partial T} = \frac{B}{T^2}$$

9. Theoretically, there are always two curves necessary to represent the complete series of equilibria, the first when the solution is saturated in respect to one substance, the second when it is saturated in respect to the other.

10. When the two non-misible substances are partially miscible with the common solvent the equation describing the equilibria is of the form: $(x+A)(y+B)^n = C$.

11. These formulæ enable us to determine whether the solvent and solute form addition products.

June 1, 1895.

NEW BOOKS.

Elektrochemie: Ihre Geschichte und Lehre. *W. Ostwald. Lexicon octavo. xvi and 1148 pages. Veit und Comp. Leipzig. 1896. Price: in paper, 28 marks; bound, 30 marks.*—After a short preliminary chapter on early experiments with frictional electricity the author enters on his subject with a full account of the discovery of Galvani and Volta and shows how a study of the chemical action of the latter's battery—curiously enough not noticed by the discoverer himself—led Davy to the preparation of the alkali metals, Berzelius to his system of chemical classification and lastly Faraday to the discovery of the law called by his name, which in determining the relation between the amount of chemical decomposition and *one* factor of the electrical energy—the «quantity» of electricity—laid the foundation of the quantitative epoch in electrochemistry. In the second half of the book, beginning with Helmholtz's introduction of the principles of Energetics and taking up in succession the work of Hittorf, Peltier, Gibbs, Kohlrausch and Lippmann he comes to a conclusion in the chapter on «the theory of electrolytic dissociation», in which the numerical connections between the electromotive force (the *second* factor) and the chemical changes in the cell—a question which from Volta's time to ours has divided the workers on this subject—is deduced from a fully developed quantitative theory of chemical affinity, resting on the laws of energetics and rendered applicable to phenomena in solutions by the work of van 't Hoff and of Arrhenius. The prominent part played by the author in the recent development of the subject lends special interest to this part of his work.

The book is illustrated throughout by some 260 cuts, reproductions of diagrams, apparatus, portraits, etc., from old books and periodicals; and the opinions of the various authors are, for the most part, given in the form of quotations from their writings, an extreme instance of this practice being afforded by the chapter on «Faraday's law», where out of a total of 102 pages, 68 are filled with extracts from the «Experimental Researches.» From original material such as this one may see for himself that a change has taken place during the past century both in the opportunities for carrying on scientific work and in the whole manner of scientific thought:—where could there be found a greater contrast to the laboratory worker of to-day than is afforded by the sketch of Galvani in puffs and knee-breeches performing his experiments in the counting house of a friend, or by the quotations from Volta, firmly convinced that he was on the high road to discovering perpetual motion!

Although this is the first book on history as such written by Professor Ostwald, yet his views as to the importance of the historical treatment of the natural sciences are well known, being evidenced not only by the publication under his name of the « Classics of the Exact Sciences» but perhaps even more strikingly by the method adopted in his «*Lehrbuch der allgemeinen Chemie*»; and consequently it goes without saying that the present work is no mere compendium of facts and register of theories: each hypothesis as introduced is subjected to a thorough criticism both from the standpoint of the present day and from that of the writer's contemporaries, the origin of the more important theories is carefully sought—justice being done in this connection to Ritter and to Erman—and in particular the growth of the convictions later expressed in the law of the conservation of energy is traced, and the difficulties and misapprehensions met with in the application of the law when formulated are illustrated in a manner which cannot fail to be of service now that the conception has become so familiar as to seem almost axiomatic. In addition the author has considered it an important part of his work to study the various changes in scientific fashions during the past century—Ritter the «natural philosopher», whose crazy style ought to have earned him a foremost place among Nordau's «degenerates»: the next following school with its masses of undigested experimental results published as «valuable material»: Clausius with his «mode of motion that we call heat»—all are representatives of bygone styles and are treated as such, nor has the author let slip the opportunity of insisting on the moribund state of the kinetic molecular theory, and the certainty of its speedy replacement by the thermodynamic or «energetic» treatment of chemical and physical problems.

Lastly an attempt has been made by the study of the evolution of this particular branch of knowledge, to discover if possible the laws regulating the progress of scientific thought in general: and as at least as much is to be learned from the mistakes as from the more fruitful ideas of the leaders of science, there are scattered throughout the book discussions on questions such as: why did not Volta discover the chemical action of his battery?—why did Berzelius ignore and combat Faraday's results?—why had Hittorf to wait so long for recognition of the value of his work?—why was it left to the workers in *one* laboratory, Leipzig, to reap the fruit of a century's labor and solve the problem of the E.M.F.? . . . and even though the reader come to the conclusion that after all no answer to these questions has been found other than that suggested by the words «human nature», still it cannot but be useful to learn how repeatedly almost the whole scientific world has «applied itself with peculiar zeal to the repudiation of a new way of looking on things, little different perhaps from the ordinary, but able to show the way simply and clearly over a whole series of former obstacles—seeking everywhere for arguments no matter how flimsy as excuses for rejecting it, and taking rare pleasure in the endeavor to prove that things are not so simple as in the light of the new theory they seem to be: How often the progress of science has been hindered and it has been reserved for a later period to do justice—and take a lesson for itself!»

W. Lash Miller.

A Dictionary of Chemical Solubilities. *A. M. Comey. 8vo. 515 pp. Macmillan and Co., New York, 1896. Price $5.00.* In this book the author has attempted to give the solubilities of all analyzed inorganic substances. The order of arrangement is alphabetical. The compounds of the metals with the non-metallic elements are given under the metals while the salts of the oxygen and other complex acids are arranged under the acids. A uniform classification of everything under the metals or everything under the acids would have been better; but the present arrangement is the one used in other chemical dictionaries and has been adopted for this reason. The fundamental principle that a solution must be saturated in respect to something has been ignored very consistently, cupric chloride being a typical example. Inversion temperatures are rarely given and the only instance where the author has given the limits of stability for different hydrates is for manganous sulfate, the one case of all others where the data are certainly wrong. The author's method of compiling his book is an interesting one. He took all the text books with which he was familiar and looked up the references to solubility determinations. The chief drawback to this plan is that one is apt to overlook the data of the last ten years and this is very much what has happened. No one would guess from the casual remarks on iodine mono-and tri-chloride that careful solubility determinations had been made. There is nothing about the hydrates of hydrobromic acid. Roozeboom's work on sodium magnesium sulfate has been entirely overlooked as well as van der Heide's determinations of potassium magnesium sulfate. There is no reference to Meyerhoffer's second paper on the double chlorides of potassium and copper, and the first paper has evidently not been read for only one double salt is mentioned. Under lead potassium iodide Schreinemakers is not mentioned and the list of omissions might be increased indefinitely. Nor is this all. Data that are known to be wrong are quoted while no reference is made to the later work, as in the remarks on the hydrates of copper and magnesium sulfates.

The author includes the action of acids on metals under the head of solubility and justifies this by saying that the discussion between the upholders of the hydrate and the dissociation theories is not settled. This is much the same as saying that the moon is made of green cheese because it is an open question whether wood or metal is better for the frame of a bicycle. The data are interesting and valuable though irrelevant; but what is one to make of the statement that copper is soluble in a hot ferric chloride solution? Surely something more is necessary! Just why tables of specific gravities should have been included in the Dictionary of Solubilities is another point which seems to lack justification. In the Appendix there is a Synchronistic Table of Periodicals. The value of such a table depends upon its accuracy and completeness, and it is therefore a pity that the fifteenth volume of the *Zeitschrift für physikalische*

Chemie should be on record as appearing in 1895 and that the Philosophical Transactions should not be included in the list.

The book is hack work, and it is difficult to see how it could well have been much worse; but in spite of its defects, it is a useful book which every chemist will have to refer to occasionally. There is no other work on the subject and it is of the greatest assistance to have data gathered together which are now scattered throughout the literature. It is perhaps too much to ask that any one man should have the patience to collect such a mass of materials and the ability to edit it properly. The herculean part of the work has been done and it is to be hoped that, in the next edition, steps may be taken to make the book what it should be. The publishers have done their part of the work well. The book is of a convenient size and there are surprisingly few misprints.

W. D. Bancroft.

Kompendium der theoretischen Physik. *Woldemar Voigt. Large 8vo. Vol. I, 610 pp., vol. II, 810 pp. Veit und Comp. Leipzig, 1896. Price, vol. I, 14 marks, vol. II, 18 marks.*—Voigt's new work on Theoretical Physics is designed to supply within reasonable limits of space a text book in which readers already somewhat familiar with one or more divisions of the domain in question can find a connected and moderately complete treatment of it, can readily fill in the gaps of their knowledge and obtain a survey of the entire field. The chief characteristics of the plan are: consistent omission of developments having specificially mathematical character and omission of all experimental methods and data. The result is a theoretical book to be sure, but it is a book on physics, not one on applied mathematics. The form of presentation is clear, compact and strikingly independent of existing precedent—the work is not at all a servile reproduction of original papers.

The first volume deals with Mechanics and Heat. The pure Mechanics has of course little to do directly with the present physical chemistry; it is however interesting to note the introduction here of the mechanical theories of other branches of physics as subtopics (*e. g.* the kinetic theory of gases and of solutions, to cite a single example), a procedure which permits subsequent treatment of these branches independently of mechanical hypotheses. And the author makes clear (*p.* 91) that these mechanical analogies may be regarded only as such—the point so ably defended by Boltzmann in recent years.

Under the head Heat the immediate concerns of physical chemistry come to the surface. In the opening concise discussion of thermometry and the first law of thermodynamics a decided convenience is introduced in the notation $d'\mathfrak{Q}$ and $d'A$ for small quantities of heat and work proportional to the time dt; this makes clear to the eye that in

$$dE = d'\mathfrak{Q} + d'A$$

the first of the three terms is a differential while the others are not. The confusion so avoided was strongly felt by Clausius in his time, and it led C. Neumann to invent his hook-shaped *d*, which no one else has ever used,—the new notation is better and deserves general adoption. A beautifully general derivation of the second law for working systems whose state is determined by any number of independent variables leads next to the expression

$$\int \frac{d'\mathfrak{Q}}{T} \leqq 0$$

for closed cycles[1]; and, after defining specific heats and heats of change, Carnot's function T is deduced from the properties of ideal gases, and the general formulas for free energy in reversible processes are found. Then follow the thermodynamics of elastic bodies and of irreversible adiabatic changes,—where appear the theory of the Thomson-Joule porous plug experiment and the theorem of entropy-increase—and the theory of heat conduction. In the succeeding section on the general conditions of equilibrium we encounter (*p.* 564) the ingenious statement that, E' denoting inner energy and Ψ kinetic energy, we must always have

$$d'\mathfrak{Q} + d'A = dE' + d'\Psi$$

and at the outset of an action $d'\Psi > 0$, whence as condition for the beginning of an irreversible change.

$$dE' - d'\mathfrak{Q} - d'A < 0.$$

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[1] Compare Buckingham, Physical Review 4, 39 (1896).

The matter seems to be correctly stated, yet the reader gets an uneasy feeling that $d'U$ becomes negative before the close of the action, and that the relation (*p* 569)

$$dE' - TdH - d'W < 0$$

may not hold true over all paths between states which do not lie close together.

The remainder of the volume (*pp.* 566 and *ff.*) deals with the thermodynamic equilibria of systems of varying masses—chemical systems—and it follows Gibbs closely. The troublesome formulation $d'E - TdH - d'A < 0$ put at the head of the discussion is fortunately not used. Gibbs's equation

$$\sum_i \sum_k \zeta_k^{(i)} \delta m_k^{(i)} = 0,$$

where the summations are made over the components (k) and the phases (i) respectively, ζ denoting the Potential of Gibbs, the Chemical Intensity of Helm, and m the mass, is properly made to comprise the entire equilibrium theory. It seems unfortunate that Gibbs's symbol μ for the potential has been replaced by the ζ used by him for a different quantity. Gibbs's theorem that a potential must have uniform value throughout a system for equilibrium, his phase rule and the differential properties of the thermodynamic potential are derived and clearly discussed in order. In stating the relations obtaining between pressure and temperature for systems of different variance (*pp.* 572–3) the corresponding relations involving the potentials, and consequently the concentrations, have been overlooked. One-component systems, including the Theory of Continuity and the relation between vapor pressure and surface tension, are treated beautifully; the reviewer notes with pleasure (*p.* 583) a favorite idea that fusion boundary curves may possibly terminate with the appearance of critical phases. There is no notice of the temperature-maxima af such curves, as observed by Damien. It is pleasing also to find van der Waals's equation termed an interpolation formula; Gibbs's thermodynamic surfaces, namely the

$(\eta - v - \epsilon)$, $(t - v - \psi)$, $(\eta - p - \chi)$, $(t - p - \zeta)$ and the $(m - \zeta)$

surfaces, should have been mentioned. For systems of more than one component there appear the theory of dissociation equilibria, essentially Gibbs, and the van 't Hoff theory of solutions. This concludes the volume.

The second volume is devoted to Electricity, Magnetism and Light. An immense amount of ground is covered, that most interesting to the readers of this journal is naturally the section on electrolytic conduction and the electromotive forces of the various types of voltaic cells.

The work as a whole gives probably a more comprehensive and connected brief exposition of theoretical physics than can be found anywhere else, and it is happily so written as to require only ordinary mathematical equipment for its reading. The citations are well chosen throughout, but are inconveniently placed at the close of the several parts of the volumes. The handsome finish of the work is a credit to its publisher and a comfort to the reader. Taking all together we have here to do with an unusually careful, comprehensive and reliable book.

J. E. Trevor.

The Molecular Theory. *J. E. Trevor. Andrus and Church, Ithaca, 1896.*—An exposition of the theory of molecular formulas, accompanied by seventy practical problems illustrating the use of this theory in general chemistry. Designed to serve as a problem-book to accompany elementary courses of instruction in general chemistry.

REVIEWS.[1]

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

General Theory and Thermodynamics.

Thermodynamic Properties of Air. Part II, Specific Heat. *A. W. Witkowski, Phil. Mag.* **42,** *1 (1896).* Calorimetric determinations of the specific heat of air under atmospheric pressure at different temperatures. This specific heat is shown not to vary sensibly from the value 0.2372 between +100° and −170°*C.* General thermodynamic relations are then employed in the calculation of the specific heats at constant pressure and at constant volume for different pressures and temperatures, and in finding the ratios of the two at different temperatures and densities. The isothermal specific heats at constant volume are found to be, within wide ranges of temperature and pressure, linear functions of the pressure.

J. E. T.

On a New Theory of Capillarity. *Marcellin Langlois. Comptes rendus,* **123,** *35 (1896).* Comment on a memoir submitted to the French Academy. The author announces that after four years of minute researches, in which all chemistry has been passed in review, he has succeeded in establishing the distribution of the inner energy of the atoms of bodies. He states the specific heat to vary with the temperature because «there can appear dissociations of hypoatomic elements», and that he has determined the «laws of explosion, of dissociation . . . . and the fundamental law of the surface tensions of liquids.» *J. E. T.*

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[1] The increased amount of space devoted to original articles in the present issue has necessitated the displacement of many of the current reviews into the November number. THE EDITORS.

The Teaching of Beginning Chemistry. *Paul C. Freer, Science,* 4, *July 31 (1896).* In the present state of much of the elementary instruction in general chemistry it is peculiarly refreshing to meet so straightforward an exposition of sensible views as has been recently published by Professor Freer of the University of Michigan. Briefly it is somewhat as follows: The momentous changes which have been brought about in chemical science within the past two decades are often lost sight of in teaching the elements of this subject. It is easier to go the old way, the habit of descriptive chemistry as founded primarily upon the atomic hypothesis is too well established to be suddenly uprooted. The undue emphasis too often laid upon analytical chemistry is a remnant of Berzelius's time, the chemical field has now become so widened that many other branches of the science have far outgrown analysis in relative importance. It is time to bring the teaching of chemistry to a more purely experimental basis, and to omit theoretical deductions, especially the atomic theory, until the pupil disposes over sufficient material to give them definite meaning. Whether we hold to the atomic hypothesis or not, the laws of definite and of multiple proportions make chemistry a quantitative science, and this aspect should be brought out in the elementary laboratory instruction; qualitative experiments can often be altered to quantitative ones by the simple graduation of a glass tube, quantitative experiments in the neutralization of acids and bases can be readily carried out,—and the reviewer has found it of advantage also to require for practice the simultaneous reduction to standard conditions of two volumes of a mass of gas, measured successively under widely differing conditions of temperature and pressure, to bring out clearly the significance of the simple laws of gases. The early use of the atomic hypothesis is confusing and pernicious, giving, as it does, a visionary basis for the science, which is too apt to cling to the pupil throughout his subsequent course.

Teacher and pupil must recognize from the start that there are two enduring things in the universe—matter and energy—and that but half the tale has been told when, in studying a chemical change, only the former has been considered. An elementary knowledge of chemical equilibrium, of dissociation in solution, of the separation of ions by the electric current, and of the modern views of neutralization, is now as essential to the beginning of chemistry as in any descriptive matter; and the pupil's work should be centered around observed facts. Such a course of study to be successful need take up but a few of the more important elements and compounds; the time for the study of all the elements and of their relations in the periodic system is not in the beginning. «I have known of teachers who required their students to balance large numbers of equations, outside the laboratory and according to set rules, and thus entirely subvert the purpose of chemical notation—to express observed facts—and lead the beginner to the conclusion that reactions must actually take place exactly as the equation demands».

[Ideas such as these are unquestionably spreading. The scientific superstition and false conservatism which have largely prevailed for a long time in the elementary teaching of chemistry is shocking and cannot last. True conservatism and a tender regard of facts are taking their places. Before leaving the present paper however it should be observed that although «chemical formulas in their present meaning are founded on the atomic theory», yet they are to be used not in this supposed *present* meaning but in their *real* meaning of combining and molecular weights as made definite by the laws of definite and multiple proportions and the volume-combination law of Gay-Lussac; no molecular or atomic conceptions are involved in this. And, further, that «matter and energy are two enduring things in the universe» is a tenacious old error. The energy doctrine is a scientific *method*, it is one of many possible methods, the conception of a *substantiality* of energy is nonsense.[1] This however weakens in no wise the argument of Mr. Freer.]

J. E. T.

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[1] This exceedingly important matter is most lucidly put in Mach's famous paper on the conservatism of energy, which may be read in English translation in Mach's *Popular Scientific Lectures, Chicago, 1895.*

Qualitative Equilibrium.

On the Liquation of Certain Alloys of Gold. *E. Matthey. Nature,* **54**, *(July 16), 256 (1896).* Alloys of gold with lead and zinc contain more gold in the centre than in the surface of the spherical ignot. An alloy containing 10 per cent zinc, 20 per cent lead, 20 per cent silver and 50 per cent gold solidified to a homogeneous mass. The author has overlooked the important discovery of Roberts-Austen that such alloys are more homogeneous when cooled slowly. *W. D. B.*

On the Effect of Molecular Bombardment on the Diamond. *W. Crookes. Chem. News,* **74**, *39 (1896).* When a diamond is placed in a Crookes tube it becomes black on the surface in the course of time. This blackening is due to the formation of graphite and is not affected by ordinary oxidizing reagents. Some diamonds which had been blackened in this way are thought to have become less black in the course of years. This would be very interesting if true but needs further confirmation. The idea of the author that the change from graphite to diamond would be affected by the relative masses of the two substances is of course erroneous.

W. D. B.

Substances exhibiting Circular Polarisation both in the Amorphous and Crystalline States. *W. J. Pope. Jour. Chem. Soc.* **69**, *971 (1896).* Cis. π-camphanic acid is optically active both in solution and in the crystalline form. The crystals are always laevorotary and the circular polarisation can not be due to lamellar structure. With trans. π-camphotricarboxylic acid the behavior of the crystals can best be explained by the theorem of Reusch.

W. D. B.

On certain Views concerning the Condition of the Dissolved Substances in Solutions of Sodium Sulfate. *R. F. D'Arcy. Jour. Chem. Soc.* **69**, *993 (1896).* Solutions of the same concentrations were found to have the same viscosity whether prepared from the decahydrate, the heptahydrate or the anhydrous salt. As no one disputes this, the paper is superfluous. No change in the viscosity was found after heating and cooling the solution. If any change had taken place the author would not have been able to detect it unless the reaction velocity had been extraordinarily low.

W. D. B.

Liberation of Chlorin during the Heating of a Mixture of Potassic Chlorate and Manganic Peroxide. *H. C. McLeod. Jour. Chem. Soc.* **69**, *1015* (*1896*). It is shown that small amounts of chlorin are formed in addition to oxygen, but no ozone. Unless special precautions are taken, the oxygen carries with it very perceptible traces of solid potassium chlorid. *W. D. B.*

The Rotation of Aspartic Acid. *B. M. C. Marshall. Jour. Chem. Soc.* **69**, *1022* (*1896*). The author confirms the statement of Piutti that ordinary asparagin yields a dextro-aspartic acid and a laevo-malic acid, while dextro-asparagin can be converted into laevo-aspartic acid and then into dextro-malic acid. *W. D. B.*

On the Use of Antimony Trichloride in the Synthesis of Aromatic Ketones. *W. J. Comstock. Am. Chem. Jour.* **18**, *547* (*1896*). Antimony trichlorid can often be used in the Friedel and Crafts reaction instead of aluminum chlorid. The yield is about the same in the two cases. The antimony compound is cheaper and more convenient to handle; but the use of it seems to be limited to the preparation of ketones. *W. D. B.*

The Atomic Weight of Japanese Tellurium. *Masumi Chikashigé. Jour. Chem. Soc.* **69**, *881* (*1896*). Brauner's tetrabromid method, applied by him to tellurium found in combination with metals, was used by the author with tellurium of a very different origin, namely a massive, red Japanese sulfur containing selenium. The value 127.6 is found for the atomic weight, in close agreement with the results of Staudenmaier, 127.6, and Brauner, 127.64.

J. E. T.

On the Solubility of Carbon in Rhodium, Iridium and Palladium. *Henry Mosssan. Comptes rendus*, **123**, *16* (*1896*). These three metals, like platinum, dissolve a small percentage of carbon readily at the temperature of the electric furnace. They precipitate it as graphite before solidification and do not form carbides. *J. E. T.*

On the Action of a High Temperature upon certain Sulfides. *A. Mourlot. Comptes rendus,* **123**, *54* (*1896*). The sulfids of lead, antimony, zinc, and cadmium have been obtained in crystallized form by either melting or subliming them in the electric furnace. *J. E. T.*

Researches on Tungsten. *Henri Moissan. Comptes rendus,* **123**, *13; also Ann. chim. phys.* (7) **8**, *570* (*1896*). Report on the production of metallic tungsten by the reduction of tungstic acid by carbonized sugar in the electric furnace with a current of 900 amperes at 50 volts. The metal is more infusible than chromium and molybdenum, is malleable, and when pure has density 18.7; its melting point is lowered by the addition of carbon, and with carbon in excess the carbid CTu_2 is formed. *J. E. T.*

Action of Zinc upon Photographic Plates. *R. Colson. Comptes rendus,* **123**, *49* (*1896*). If a fresh surface of zinc is placed in contact with a gelatine film or is separated from it only by a layer of some porous material, the vapor of the zinc attacks the silver bromide so that the developed plate shows an image of the piece of zinc. Magnesium and cadmium give the same effect; but lead, tin, copper, iron and aluminum do not. It is probable that with longer exposure the same result can be obtained with these latter metals.

W. D. B.

Quantitative Equilibrium.

Melting Points of Aluminum, Silver, Gold, Copper and Platinum. *Holman, Lawrence, and Barr.* **The Technological Quarterly.** *Phil. Mag.* (*5*) **42**, *37* (*1896*). Assuming 1072° C. as the melting point of pure gold the authors find the following melting points by a thermo-electric method: aluminum 660°, silver 970°, copper 1095° and platinum 1760°. Samples of copper from different sources had so nearly identical melting points that this temperature is recommended as one of the fixed points in calibrating thermopiles.

W. D. B.

Relations between the Laws of Active Masses and of Osmotic Pressure. *A. A. Jakowkin. Zeit. phys. Chem.* **22,** *321 (1896).* From the two assumptions (*i.*) that in aqueous solution a hydrate of the substance dissolved (A) is formed according to the equation $A + H_2O = A \cdot H_2O$, and (*ii*) that the concentration of H_2O molecules in the solution and in pure water respectively are proportional to the vapor tension of the solution and of water at the same temperature [suggested indirectly by Henry's law], the author deduces the «vapor tension laws» for dilute solutions in the form

$$\frac{p-p'}{p} = \frac{n}{N} \cdot \frac{1}{1+kv}$$

This result is directly dependent on the formula of the hydrate, *viz.* $A \cdot H_2O$—from $A_2 \cdot H_2O$ quite a different relation would have been obtained—no reason however is given why one formula should be chosen rather than another. The equation for the vapor tension once obtained, those for the osmotic pressure, gas laws in solution and Henry's law follow without difficulty: the deduction of the «indexed Henry's law» on the other hand is not at all clear.

The author's results cannot however be considered as justifying his premises, as they may be arrived at by methods free from special hypotheses as to the nature of solution: the vapor tension law in particular can be deduced by purely thermodynamic considerations from the gas laws and the law of Henry alone, and consequently the introduction (in addition to these) of the hydrate hypothesis is wholly unnecessary. *L. M.*

Freezing-point Depressions of very Dilute Solutions. *R. Abegg. Zeit. phys. Chem.* **20,** *207 (1896).* The apparatus of Nernst and Abegg is improved by using ice and a dilute salt solution in the freezing bath; by shielding this latter on all sides with felt and wool; and by having automatic stirrers, with vertical instead of rotary motion, in the bath and in the solution. A liter of solution is used. The thermometer is divided into 1/500° and has an electric hammer attached. Some satisfactory measurements were made with various non-electrolytes and salts; but potassium nitrate and magnesium sulfate were not examined. Equilibrium is reached with potassium chlorid in half the time necessary with cane sugar.

W. D. B.

On the Solubility of Barium Sulfate. *F. W. Küster. Zeit. anorg. Chem.* **12,** *261* (*1896*). The author objects to such a phrase as «Solubility in the nascent state». He shows that Fresenius and Hintz have measured the concentration of a super-saturated solution and that the true solubility of barium sulfate is roughly one part in 425,000, as was found by Kohlrausch and Rose and by Holleman. The author also shows that most of the peculiarities found by Fresenius and Hintz can be predicted from Nernst's theory of solubility. A very interesting point comes out in this paper; that barium sulfate forms a solid solution with sulfuric acid.

W. D. B.

On a Compensation-Method in Gasometry. *C. von Than. Zeit. phys. chem.* **20,** *307* (*1896*). The principle on which the method rests is that the ratio between the volume of the gas at a given temperature and pressure and the volume of the gas at normal temperature and pressure is independent of the nature of the gas. By comparing the actual volume of the gas to be analyzed with the actual volume under the same conditions of another gas, the normal volume of which has been determined once for all, one has all the data necessary. The advantage of this method is that neither pressure nor temperature needs to be known. It is merely necessary that the pressure and temperature of the gas in the eudiometer shall be the same as that in the standard tube. When the gas to be analyzed is moist, a little water must be introduced into the standard tube.

W. D. B.

Thermochemical Data for Mercuric Cyanid. *R. Varet. Ann. chim. phys.* (*7*) **8,** *437* (*1896*). A tabulated summary of the heat effects produced by the action of the halogen salts of the alkali metals and the alkaline earths upon mercuric cyanid.

W. D. B.

A General Verification of the Corresponding States of van der Waals, *E. H. Amagat. Comptes rendus,* **123,** *30* (*1896*). «The law of corresponding states can be put in the broadest way thus: If groups of isotherms of any two substances are drawn to the same scale, pressures and volumes being expressed in terms of their critical values, the groups of isotherms should be capable of being superposed producing a single group of isotherms belonging apparently to only one substance." Therefore, it should always be possible to make a group of isotherms of one substance coincide with a group of isotherms of another substance on readjusting the units used in drawing the isotherms, by expanding or contracting the axes of coordinates. This was done by optical projection for the isotherms of carbon dioxid, ether, and air, in one case and for the isotherms of ether and ethylene in another case. The coincidence was excellent and fully supported the theory of van der Waals in these two cases. Unfortunately, such a test could not be made with other bodies for lack of data. *Clarence L. Speyers.*

Velocities.

Explanation. *R. Wagner. Zeit. phys. Chem.* **20**, *334 (1896).* A statement that in an earlier paper on the velocities of decomposition of the nitrogen-sulfur-acids, the allied work of Hantzsch and of Divers was overlooked. The author promises to recur to the subject. *J. E. T.*

On the Esterification of Halogen-substituted Acids. Second Paper. *D. M. Lichty. Am. Chem. Jour.* **18**, *590 (1896).* Equivalent weights of ethyl alcohol and the acid were made to react for definite intervals at 18°C. After cooling, the free acid was titrated with ammonia in presence of rosolic acid. The mean percentage of each acid converted is expressed in tables, and these data are presented graphically through smooth curves whose general form agrees with the theory for reversible reactions. The limit in each case and the influence of the substituted chlorin may be assumed as follows:

Acid	*Limit*	*Increase*
Acetic	66.57	——
Monochloracetic	68.65	2.08
Dichloracetic	71.22	4.65
Trichloracetic (about)	74.	7.5

The initial rate of change (as given in the table for one minute) for dichloracetic acid is 2.56 times, and for trichloracetic acid is 5.61 times that of monochloracetic acid. The influence of chlorin is therefore comparatively slight upon the limit of esterification but very great upon the rate in early stages. The rate of esterification depends upon two factors, one the mass-action of water *versus* alcohol, and the other the specific nature of the acid ; but the author wishes to trace similar curves for other acids before determining their mathematical expression. *Robt. B. Warder.*

On Certain Alkyl-substituted Valero-lactones. *Edv. Hjelt. Berliner Berichte,* **29**, *1855* (*1896*). Measurements of the rates of formation of the lactones from the potassium salts of the corresponding acids by the action of hydrochloric acid in aqueous solution. Each solution contained per liter 0.055 mol. wt. in grams of the salt and an equivalent quantity of hydrochloric acid. The reaction is bimolecular, and its progress (measured by titrating residual acid by fiftieth normal potash) agrees with the formula

$$Ac = \frac{x}{1-x} \cdot \frac{1}{t}$$

If A be set$=100$, and x consequently the per cent of lactone formed after t minutes, the following are the values for Ac:

γ-oxyvaleric acid	0,0027
Isopropyl γ-oxyvaleric acid	0,0085
Propyl γ-oxyvaleric acid	0,0100
Ethyl γ-oxyvaleric acid	0,0104.

L. M.

On the Velocity of the Formation of Lactones from Certain Acids of the Sugar Group. *Edv. Hjelt. Berliner Berichte* **29**, *1861* (*1896*). Each solution contained per liter 1/25 gram molecule of the sodium salt of the acid and an equivalent quantity of hydrochloric acid. The experiments were carried on at 52°C. and the progress of the reaction determined by titration with fiftieth normal soda. The values for Ac (see preceding review) are in most cases far from constant. Six acids were studied. *L. M.*

ALLOTROPY OF SUCROSE.

BY F. G. WIECHMANN.

Solid sugar (sucrose) is known to exist in two allotropic modifications, the crystalline and the amorphous.

The properties of crystalline sucrose are too well known to require enumeration. Amorphous sucrose is obtained by slowly melting pure crystalline sucrose, carrying the temperature to about 160° C. and then allowing the melt to cool. The amorphous product resulting is a transparent, vitreous and optically active solid. Amorphous sugar is more readily soluble in water than the crystalline modification ; it is a poor conductor of electricity ; its specific gravity is, according to Graham, 1.5090.

Although this substance can be kept unchanged for some time, yet its condition seems an unstable one and the tendency exists to return, sooner or later, to the crystalline form. Recently the writer had occasion to study, to a certain extent, this transformation of amorphous sugar and, as some of the observations made are new and possibly of interest, they are here given.

The amorphous sugar was made in two ways.

A. Refined crystalline sugar was put into an open copper vessel and about one-third its weight of water added. Under constant stirring the solution was heated to boiling in about five minutes time. The vessel was then covered with a clock-glass and boiling continued for ten minutes longer. Then the clock-glass was removed and the temperature of the solution raised to 176° C. As soon as this temperature was attained, the vessel was removed from the flame, and its contents quickly poured on a copper slab and there allowed to cool.

B. This method of preparation was identical with that just described, except that there was added to the water in which the sugar was dissolved, either some calcium oxide, sodium mono-carbonate or sodium bi-carbonate. The amount of these reagents added was one part to one hundred thousand parts, by weight, of the sugar used.

In every instance the slab of amorphous sugar obtained was cut into small plates 8 *cm.* long, 3 *cm.* broad and about 0.5 *cm.* in thickness. These plates were put into glass flasks and the latter securely corked.

Following are the analytical determinations made on the sugars used and on the amorphous sugars produced.

No.	Method	Reagent added	Polarization of sugar used	Amorphous Sugar	
				Polarization	Reducing Sugars
1	A.	None	97.9	91.3	6.90
2	B.	Na_2CO_3	97.9	95.8	1.84
3	B.	$NaHCO_3$	97.9	96.1	1.59
4	B.	CaO	97.9	95.9	1.82
5	A.	None	98.0	92.4	5.41
6	B.	Na_2CO_3	98.0	95.9	1.59
7	B.	$NaHCO_3$	98.0	95.8	1.61
8	B.	CaO	98.0	95.7	1.85
9	A.	None	97.9	68.6	28.60
10	B.	$NaHCO_3$	97.9	95.8	2.50
11	B.	$NaHCO_3$	97.9	95.9	1.51

In each of these experiments the specimens were put up in duplicate, one being exposed to daylight, the other being kept in darkness.

The question whether the color of the light to which the specimen was exposed would exercise any appreciable influence on the result was tested with No. 11 of the series. Three samples of this specimen were taken. One was placed in a flask made of pure white glass, the second was put up in a flask made of green, and the third in a flask made of dark-blue glass and then exposed to daylight.

All of the specimens were inspected from time to time, and though in nearly all cases where the amorphous sugar passed into the crystalline form, this had been accomplished in from eight to twelve days after the amorphous sugar had been made, yet the specimens were kept under observation for two months and a half, when the following results were noted.

In *all* cases where method *A* had been employed, there was no transformation into the crystalline form. On the other hand, in *all* cases where method *B.* had been used in making the amorphous sugar, the same had been changed completely into the crystalline modification. This was true of the specimens which had been kept in the dark as well as of those which had been exposed to daylight. It held equally well for the specimens preserved in the colored flasks.

In specimens Nos. *1*, *2*, *3*, and *4*, a redetermination of the reducing sugars was made at the end of the experiments. The amounts of reducing sugars found—expressed as invert sugar, were :

No.	Originally	After 2½ months.
1	6.90	6.90
2	1.84	1.92
3	1.54	1.72
4	1.82	2.00

These figures show that the composition of the material remained practically unchanged.

Wherever crystallization occurred it was observed to start from one or more points in the plate and to radiate from these points as centres, giving rise to perfectly circular forms.

In order to study this circular, radiate crystallization more carefully a plate of amorphous sugar was specially prepared for the purpose.

Two hundred and twenty-seven grams of best refined sugar were dissolved in eighty-seven grams of distilled water to which 0.0027 gram of sodium bi-carbonate was added. The work was carried out exactly as previously described. The plate of amorphous sugar was laid on some glass rods under which there had been placed a sheet of black glazed paper, to facilitate observation. The whole was covered with a large bell-jar, and a dry atmosphere was ensured by the use of calcium chloride.

The plate was placed in front of a large window with exposure to the southwest. Inspection was made daily and the observations noted follow.

The first appearance of a crystalline nucleus—a mere point to the naked eye—was made on the tenth day following the making of the plate. Crystallization started in on the lower side of the plate and gradually extended up into the amorphous mass. Growth continued regularly and in perfectly circular form.

The measurements, across the upper surface of the crystalline disk, were taken at certain intervals, the time being counted from the day of making the plate.

	Diameter in *mm*.
After 15 days	2.00
" 25 "	5.50
" 32 "	13.00
" 34 "	15.00
" 39 "	20.00
" 41 "	22.25
" 44 "	25.00
" 47 "	28.00
" 50 "	32.00
" 54 "	35.50
" 57 "	38.00
" 61 "	42.00
" 64 "	46.00
" 69 "	51.00
" 74 "	56.00

When the disk had reached this stage of development the photograph accompanying this article, was taken. The amorphous part of the plate was a pale yellow in color and perfectly transparent; the crystalline disk was of a pure white, and barely translucent.

After the photograph had been secured, the disk was removed unbroken from the amorphous mass in which it lay embedded. Measurements made on the former were as follows:

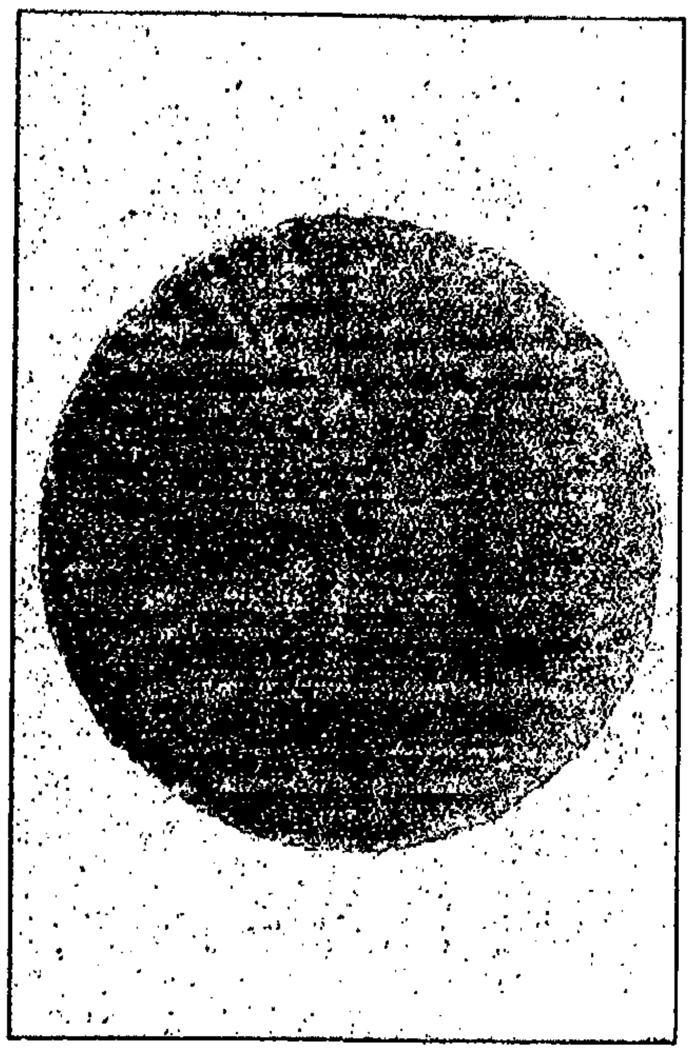
Diameter of upper face	56.00 *mm.*
Diameter of lower face	57.50 *mm.*
Thickness	4.00 *mm.*
Weight	14.98 grams

When examined with a magnifying glass the disk proved to be a beautiful structure formed by the aggregation, in radiate shape, of numerous crystals. These individual crystals were ranged one above the other, suggestive in their appearance of the blades of a fan. They were so closely and thickly matted together, that it was impossible to obtain measurements of their angles and faces.

A careful analysis was however made by the writer's method[1] of the crystalline disk and of that part of the plate which yet remained in the amorphous condition. Results were as follows :

	Crystalline.	*Amorphous.*
Sucrose	95.94	96.56
Dextrose	1.12	0.96
Levulose	0.97	0.94

These figures demonstrate the practical identity in chemical composition of the two allotropic modifications.



The question as to the cause or causes of allotropy in compound substances is an interesting one and one that has not yet been conclusively answered.

It is held that the production of allotropic modifications and the transformation of one modification into another are effected, as a general rule, by changes of temperature.[2] Raising a substance to a high temperature and then cooling it quickly to a temperature below that of transformation is conducive to the production of unstable modifications. Such unstable states can be exhibited by solids as well as by melted and dissolved substances.

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[1] School of Mines Quarterly, Columbia University. Vol. XIII. No. 3.

[2] Watt's Dictionary of Chemistry. Revised by Muir and Morley. 2nd Edition. Vol. I. p. 128.

It has been determined by Flourens[1] and by Weitz,[2] that the slow cooling of a sugar solution concentrated at 140° C. produces vitreous, amorphous sugar, whereas a brisk stirring of the mass causes a marked rise in temperature, evaporation of water ensues and a crystalline powder is formed.

It is also well known that light, or some other form of energy accompanying light, may induce transformations from one allotropic state into another.[3]

In these experiments, however, it is evident that the change from the amorphous to the crystalline state can not be ascribed to the action of light, for the specimens kept in the dark experienced the change as well as those which had been exposed to light. Neither can these transformations from the one state to the other be ascribed solely to the changes in temperature by which the amorphous sugar was produced, for, in this respect, all were treated alike; yet some specimens suffered the change while others did not.

The only point of difference between those specimens of amorphous sugar which turned into the crystalline condition and those which remained in the amorphous state, was, that the former, without exception, contained a trace of foreign inorganic matter, while the latter did not.

It would thus seem difficult to escape the conclusion that these minute amounts of foreign substance had, by their presence, imparted sufficient of an impulse to the sugar molecules to cause the same to seek and to attain a more stable state of equilibrium—the crystalline modification.

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[1] Comptes Rendus **83**, 150.

[2] Oesterreichish Ungarische Zeitschrift für Zucker-industrie und Landwirthschaft, **8**, 405.

[3] Wiechmann, Photo-crystallization. School of Mines Quarterly, Columbia University, Vol. XVII. No. 1.

NASCENT HYDROGEN.

BY R. FRANCHOT.

Fourteen years ago Thorpe[1] published some very interesting measurements on the reduction of ferric sulfate in acid solutions by magnesium and zinc. It appeared that, for equal reacting weights of magnesium and zinc dissolved, there was three to four times as much ferric sulfate reduced with zinc as with magnesium. This seemed to prove the existence of a specific reducing effect due to the metal attacked; but Thorpe recognized that the experiments were inconclusive for the following reason. The time necessary to dissolve one reacting weight of magnesium is much less than the time necessary to dissolve one reacting weight of zinc, the surfaces of the metals in contact with the solutions being the same in the two cases. As other experiments showed that increased reaction velocity meant decreased reduction of ferric sulfate, Thorpe decided that the discrepancies between the reducing powers of magnesium and zinc were probably due to the different rates at which these two metals dissolved. While this conclusion may be correct it is no more proved than the preceding one. At the request of Professor Bancroft, I took up the work at the point where it was left by Thorpe with the intention of settling the question whether the nature of the metal acted upon has any effect upon the reducing power of the hydrogen formed. The research developed rather differently than had been expected so that, with the limited time at my disposal, I was unable to reach any satisfactory conclusion on this point though I have obtained some results which bear upon the problem.

In order to eliminate the effect due to the different reaction velocities, it is necessary to have the metals dissolve at the same rate. There are two ways of doing this. Different amounts of surface might be exposed by having one metal in the form of heavy wire and another in thin plates. In this way it would be possible to

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[1] Jour. Chem. Soc. 41, 287 (1882).

have the two metals dissolve at nearly the same rate; but this would be very cumbrous and inaccurate. The other way, which has been adopted, is to avail oneself of Faraday's Theorem that a given current dissolves equivalent amounts of different metals in the same time provided there are no secondary reactions. As it was impossible to apply this method to magnesium, the metals zinc, cadmium and copper were taken. Ordinary amalgamated zinc was used and also some sticks of very pure zinc from the chemical museum; the cadmium was the purest stick cadmium of commerce and was obtained from Eimer and Amend. It was not amalgamated. For the copper electrode heavy wire was taken. The method employed was to set up three cells in series in three beaker glasses with zinc, cadmium and copper as anodes and the same quantity of a known solution of ferric sulfate and sulfuric acid in each beaker. The reaction was hastened by connecting the three cells with the dynamo-current supplied to the laboratory. By measuring the loss of weight of the anodes, there could be calculated the total amount of hydrogen which might have been given off, while a determination of the ferrous sulfate formed gave the amount which had been used for reducing purposes. At first mercury was used as the cathode; but it was found that the results were very irregular. This proved to be due to the transference of the metal of the anode to the cathode. As soon as the concentration of the zinc sulfate, for instance, around the cathode reaches a definite value, it becomes possible to precipitate zinc and hydrogen while with copper sulfate, copper only would be precipitated under proper conditions of electromotive force and current-density. The mercury electrodes were accordingly replaced by platinum because a precipitation of zinc, cadmium or copper could be more easily detected under these circumstances. The platinum electrodes were placed in beakers distinct from those containing the anodes so as to avoid the presence of salts of these metals at the cathodes. The results were not satisfactory even then for it was found that the decrease in weight at the anodes was not proportional to the reacting weights of the metals employed and that the percentage of hydrogen oxidized varied with each experiment. Under these circumstances the measurements are not comparable and indeed have no significance, so that I shall not communicate them. Since some secondary reaction was evidently taking place, it was decided to analyze the liquid round the anode. It was found that the reduction was equal to and in some cases greater than the reduction at the cathode. This made matters clear at once. It was evident that zinc, cadmium and copper reduced ferric sulfate directly. To test this a solution of ferric sulfate was carefully neutralized with sodium hydrate. To different portions of this solution, zinc, cadmium and copper were added. At the end of a few hours the solutions were poured off, acidified and titrated with a permanganate solution. In all three cases very considerable quantities of ferrous iron were found, showing the direct reducing action of the metals. With zinc and cadmium this is not surprising after one knows that it happens. Both these metals stand above iron in the electrochemical series and should precipitate it from solution just as copper does silver. The metallic iron thus formed would react with the ferric sulfate forming the ferrous salt. It is not clear why copper should act in this way nor is it certain that it does. It may be that with all three metals the reaction takes place directly and not in two stages even with zinc and cadmium. For the present the mechanism of the reaction is not important; but merely the fact that a reaction takes place. This explained the discordant results hitherto obtained. No special pains had been taken to insert the anode exactly the same distance into the liquid each time. As the amount of the direct reduction is proportional, among other things, to the surface of the metal in contact with the solution the results would naturally vary. Any states of stress in the different portions of the cast metal would influence the reaction velocity. Unfortunately this source of error was not discovered until too late in the year to make a series of determinations in which this was avoided.

From some measurements upon the reduction of potassium chlorate by the action of sulfuric acid on zinc, cadmium and copper it seems probable that these metals act directly upon the chlorate part of the salt though this was not definitely established. There is nothing improbable in this. Gladstone and Tribe[1] found that zinc reduces potassium nitrate directly. I give their description of the experiment verbatim. «A boxwood cell was cut vertically into two equal parts, some pieces of parchment paper were placed between these,

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[1] Jour. Chem. Soc. **33**, 144 (1878);

and the divisions of the cell held firmly together by a clamp. A solution of nitre was placed in each of the divisions, a strip of zinc being placed in one, a strip of platimum in the other. The strips were connected together by a metallic wire, and allowed to remain so for two to four days, the action being a feeble one. The general result of several experiments was, a little ammonia in each of the divisions ; free potassium hydrate in the platinum one, none in the zinc ; and about ten times less nitrate in the platimum than in the zinc division.» The reduction of the potassium nitrate and the formation of caustic potash in the platinum division are due to electrolysis and nascent hydrogen. The reduction in the zinc division is due to the direct action of the metal. A piece of the same zinc was found to reduce potassium nitrate when no platinum was present. Part of this effect was due to impurities in the zinc setting up local galvanic action ; but granulated, redistilled zinc behaved in the same way though the reduction was a good deal less. Some experiments on the electrolysis of potassium nitrate between zinc and platinum electrodes induced Gladstone and Tribe to reject this explanation, unwisely as it seems to me. Gladstone and Tribe[1] have also found that spongy lead reduces potassium nitrate ; and potassium chlorate when a little sulfuric acid is present. This is in accordance with the results of Johnson[2] who found that finely divided copper did not reduce aqueous potassium chlorate. He did not try the effect of adding acid. More recently Tower[3] has found that zinc acts upon zinc nitrate though the nature of the reaction was not investigated. The same result was found by Neumann[4] to be the case with all metals in solutions of their nitrates. Higley and Davis[5] have concluded from their investigations upon the action of nitric acid on metals that direct reduction must take place though they did not establish this point very satisfactorily.

Returning to the reduction of ferric salts in acid solution in the presence of a metal, usually zinc, it is clear that two reactions go on simultaneously ; the direct reduction of the ferric salt by the metal and the indirect reduction due to the action of the acid on the metal. There

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[1] Jour. Chem. Soc. **43**, 347 (1883) ; [2] Ibid. **35**, 240 (1879).
[3] Zeit. phys. Chem. **20**, 204 (1896) ; [4] Ibid. **14**, 193 (1894) ;
[5] Am. Chem. Jour. **18**, 587 (1896).

is no reason to assume that the first reaction is not a quantitative one. That the second is not a quantitative one is shown by the fact that hydrogen is evolved experimentally. Any circumstances which increase the amount of the first reaction relatively to that of the second will increase the amount of reduction per unit quantity of metal going into solution. This can be tested by means of Thorpe's data. Increasing the surface of the metal exposed, increasing the concentration of the ferric sulfate and decreasing the amount of free acid are all changes which promote the direct reduction and Thorpe found that the reduction per unit quantity of metal dissolved was increased by each of these three changes. The last two changes not only promote the direct reduction but decrease the indirect reduction, while a change in the surface of the metal accelerates both reactions though not necessarily to the same extent. In accordance with this it was found that increasing the surface of a sheet of zinc three-fold only increased the percentage of hydrogen retained to that assumed to have been evolved some 5%. Increasing the concentration of the ferric sulfate five-fold much more than doubled the percentage of hydrogen oxidized. The effect due to the change in the concentration of the free acid is not as great as one would expect but this may be due to the hydrolysis of the ferric sulfate. On the other hand, the more readily a metal is attacked by acid, the greater will be the indirect reduction and the amount of reduction per equivalent of metal going into solution will be decreased. Experimentally the amount of oxidized hydrogen at 25° is 6.5% with magnesium, 26.7% with zinc, and 40.7% with iron under the conditions of the experiment. Wrapping the metal to be dissolved in a platinum wire forms a galvanic couple, increasing the rate at which the metal is dissolved. This should decrease the amount of effective hydrogen. This is the case with zinc though the effect is not very marked. With magnesium and iron, on the contrary, there is a slight increase in the reduction. It is not clear to what this can be due. It is possible that the platinum might increase the effectiveness of the indirect reduction. The well-known catalytic action of the platinum lends possibility to the hypothesis ; but one would expect this action to manifest itself with zinc. This point, which was left unexplained by Thorpe, needs further investigation. Another curious result found by Thorpe, is that the presence of zinc sulfate increases the reaction of velocity and decreases the amount of reduction. A given weight of zinc will dissolve more rapidly in an acid of given volume concentration if some zinc salt be added to the solution. This result is so unexpected that it seems as if there must be some error in the measurements.

It is impossible to predict the effect of an increase of temperature upon the amount of reduction per equivalent amount of metal dissolved without further measurements. The direct action of the zinc, for instance, upon the ferric sulfate will be increased while the free acid will attack the metal more rapidly. Until there are determinations of the relative changes of these two velocities there are no data upon which to base an opinion. A further complication comes in with the possibility that the percentage amount of indirect reduction may be a function of the temperature. Experimentally Thorpe found that at high temperatures more ferric sulfate was reduced for equivalent quantities of magnesium and zinc than at low temperatures while the contrary is true of iron.

Since there are two reactions taking place simultaneously when an acidulated solution of a ferric salt acts upon zinc, it is evident that the only way to get a clear idea of what is taking place is to separate these reactions so that each can be studied by itself. This can best be done by arranging the system as a two liquid cell, measuring the current and analyzing the solutions round the anode and the cathode. If the effect due to nascent hydrogen is all that is to be studied, the substance to be reduced can be placed round the cathode only and the current calculated from the loss in weight of the anode.

The results of this investigation are :—

1. A solution of ferric salt is reduced directly by zinc and other metals.

2. An acid solution of ferric salt is reduced indirectly by the action of the acid on zinc or other metals.

Cornell University, Aug. 1, 1896.

ON IRREVERSIBLE CELLS.

BY A. E. TAYLOR.

Continued from page 20.

It thus became of interest to see whether the two cells, Cd | KCl | KI | Cd and Cd | $CdCl_2$ | CdI_2 | Cd, would give the same value. We have for the electromotive force of the cells Cd | KCl | Hg, Cd | KI | Hg, Cd | $CdCl_2$ | Hg and Cd | CdI_2 | Hg respectively the values 0.815, 0.514, 0.814 and 0.514 volts. This would make the potential difference between cadmium in potassium chloride and cadmium in potassium iodide about 0.15 volts, and Paschen finds about that difference between the single potential determinations. If this is due to the change of negative ion we would also expect a current of equal value to pass in a cell from cadmium chloride to cadmium iodide.

The apparatus for these measurements was the same as that used by Bancroft[1] for oxidation and reduction cells, and by Neumann[2] in measuring single potential differences. It consisted of two small glass cylinders about 50 *mm.* high and 15–20 *mm.* in diameter, provided with tightly fitting rubber stoppers through which the electrodes passed. At about the height of 30 *mm.* a small bent glass tube was fused into either cylinder. The end of this tube was filled with a little roll of filter paper. The two cylinders were connected by means of a U shaped tube, filled with an electrolyte, into either end of which the side tubes dipped.

The first measurements were made with cadmium salts. No current could be be detected or at most a slight one, and that running from the iodide to the chloride. This result was obtained several times. I next tried the potassium salts, and found to my surprise the same thing as with the cadmium salts. The direct measurements of Paschen had already shown the single potential differences Cd | KCl and Cd | KI to be different. This pointed to one of two conclusions;

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[1] Zeit. phys. Chem. **10**, 387 (1892).

[2] Ibid. **14**, 208 (1894).

either there was something wrong with the apparatus, or the potential difference between the solutions could not be neglected and had a value something over 0.15 volts. This last view seemed highly improbable. The easiest explanation would be that of diffusion, as I had used one of the two electrolytes in the connecting U tube. To obviate this difficulty I next tried pure water in the connecting tube; thinking that, when a slight amount of salt had diffused in, I would obtain the desired reading, but the result was the same as before.

I next put mercury into the connecting tube with potassium chloride and potassium iodide in either arm, thus making a combination of the two cells $Cd|KCl|Hg$ and $Cd|KI|Hg$ and obtained the value 0.3 volts, as expected, the current going from the chloride to the iodide. I then substituted the tube containing potassium chloride, and obtained a value of almost zero as before, a very slight current running from the iodide to the chloride. On again using the tube containing mercury, the same value 0.3 volts was observed, thus disproving the assumption that there might have been sufficient diffusion to make the single potentials equal on either side. I found it to be immaterial whether water or one of the electrolytes was used in the connecting tube, as after a minute or two the water conducted sufficiently well to give practically the same value as when the electrolyte was used. These same experiments were repeated with cadmium chloride and cadmium iodide, and gave exactly the same results as the potassium salts.

To make exact measurements with two polarizable cells combined is rather difficult for the iodide cells are slower in coming to their maximum constant reading than the chloride cells, while the chloride cells polarize somewhat more quickly. By using two connecting tubes containing mercury, I was able to measure the two cells $Cd|CdCl_2|Hg$ and $Cd|CdI_2|Hg$ separately. On connecting the mercury in the two tubes by means of a platinum wire, I obtained the value for the cells combined, and by using one connecting tube containing either cadmium chloride or cadmium iodide the value of the cell $Cd|CdCl_2|CdI_2|Cd$. The following is a fair example of the measurements made. The cell $Cd|CdI_2|Hg$ having been set up for some time had come to its maximum giving the reading 0.512 volts. The cell $Cd|CdCl_2|Hg$ had just been set up and gave the value 0.812 volts. By connecting the two with a platinum wire 0.304 volts was obtained as the difference between the two cells. On using the connecting tube containing cadmium chloride 0.02 volts was obtained, the current running from the iodide to the chloride. The iodide and chloride cells were measured again and gave the values 0.512 and 0.819 volts respectively. This last cell, measured half an hour later, gave the value 0.817 volts.

Similar measurements with potassium chloride and iodide gave the same results, except that a slightly larger current, about 0.04 volts was observed to pass from the iodide to the chloride. These results force us to the conclusion that the potential difference KI|KCl has a value of something over 0.15 volts, if we accept the measurements given by the dropping mercury electrodes. Further, it would be rendered very probable that $CdI_2|CdCl_2$ has nearly the same value. This would make the measurements of Neumann, except those on the chlorides, of no value; for the single potential difference B before mentioned could not then be neglected.

The value given by the cell Hg|KI|KCl|Hg, however, does not support this view. From the measurements of Paschen we would expect an electromotive force of about 0.15 volts, the current passing in the cell from the iodide to the chloride. The electromotive force measured, is 0.362 volts. If we assume that the potential difference KI|KCl is about 0.2 volts, the electromotive force should have approximately this value. If this potential difference between the liquids does not exist, then the measurements made by the dropping mercury electrodes contain an error. The measurements of Brandenburg[1] point quite strongly to the fact that this liquid potential difference does not exist. He found that on adding to the cell $Zn|n/10H_2SO_4|Hg$ an equal volume of n/10KI, n/10KBr or n/10KCl, the electromotive force fell from 1.430 volts to 0.841, 1.050 and 1.190 volts respectively. Brandenburg explains this by the formation of the complex salts K_2HgI_4, K_2HgBr_4 and K_2HgCl_4, and the consequent decrease of the mercury ions in the solution. For the corresponding cells containing no sulphuric acid, Bancroft obtains the values 0.846, 0.990 and 1.151 volts. It would therefore seem that the formation of complex salts might explain the variation attributed to the negative ion. The addition of a more concentrated

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[1] Zeit. phys. Chem. **11**, 552 (1893).

potassium iodide solution to the cell Zn|n/10H_2SO_4|Hg did not further lower the electromotive force, but by using a more dilute solution it was raised. This value, however, could not be raised more than to 1.295 volts even by diluting the iodide solution used to a 1/327,680th normal solution. For any particular concentration of sulphuric acid and potassium iodide, diluting the whole solution did not alter the electromotive force, thus showing it to be independent of the absolute concentration. The same things were observed for potassium chloride and potassium bromide. This shows very well the necessity of using absolutely pure salts.

Brandenburg next measured some cells of the following type Hg|Na_2SO_4+KI|Na_2SO_4|Hg. The change of potential occasioned by the halogens was 0.553 volts for KI; 0.325 volts for KBr and 0.190 volts for KCl. As there is sulphate on either side there is probably no potential difference between the solutions. From the above values we may obtain

KI—KCl=0.363 volts
KI—KBr=0.228 "
KBr—KCl=0.135 "

In the cell Zn|n/10H_2So_4|Hg the maximum lowering of the potentials by the halogens is 0.590 volts for KI; 0.380 volts for KBr and 0.240 volts for KCl or:

KI—KCl=0.350 volts
KI—KBr=0.210 "
KBr—KCl=0.140 "

In this case there is no potential difference between solutions, yet the values for cells containing two halogens agree very well with those calculated from the cells of the type Hg|Na_2SO_4+KI|Na_2SO_4|Hg. For the cell Hg|KI|KCl|Hg the electromotive force is 0.362 volts was observed, which is practically the same as the values calculated from the work of Brandenburg.

If we cannot assume any large single potential difference between halogen solutions, we are forced to the conclusion that cadmium in potassium chloride does not differ much from cadmium in potassium iodide, or in other words the negative ion has no effect on single potential differences. This would lead us to suspect that, at least in some cases, measurements made by means of the dropping mercury electrodes contain an error. It will be noticed that in no case do we have any effect apparently due to the negative ion unless mercury comes in directly or indirectly. The effect might then be due to some property of mercury rather than to the negative ion, and the formation of complex mercury salts is a possible explanation since the phenomenon has been observed only in cases where complex salts may be formed.

Gouy[1] noticed that the maximum surface tension of mercury is not the same in all solutions. The measurements of single potential differences by means of the surface tension of mercury or by the method of dropping mercury electrodes presupposes that the maximum surface tension of mercury is the same in all cases. If the same maximum surface tension is not reached in every solution the measurements are not comparable. Gouy found that when solutions of the bases, of the oxygen acids or their salts were used, the curves, formed by using as ordinates the change in height of the mercury column and as abscissae the polarization, were comparable, showed very little difference in form and had the same maximum, thus obeying the law of Lippmann. With potassium chloride, iodide, bromide, sulphocyanate and sulphide the curves varied in form and in no case had the same maximum. The change in height of the mercury column in potassium iodide solution was several centimeters less than in sulphuric acid solution. In all the cases cited the surface tension at the maximum was smaller than the normal.

Rothmund[2] determined the pressure necessary to compensate the maximum surface tension of mercury in various solutions at the maximum of polarization and found that in the normal cases the pressure required was always the same, while in the cases where complex salts might be found, viz.: sulphocyanates, sulphides, cyanides, iodides and sulphites the pressure required varied considerably and was less than the normal. He, however, found hydrochloric acid to be normal. His conclusion is that the measurement of the maximum pressure is only suited for the determination of potential differences when the surface tension has the normal value,

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[1] Comptes rendus **114**, 22, 211, 657 (1892)

[2] Zeit. phys. Chem. **15**, 1 (1894).

viz.: that observed for sulphuric acid and most other electrolytes. Luggin[1] obtains similar results. If in certain solutions the maximum surface tension of mercury is less than the normal, an error will be introduced into the determinations with dropping mercury electrodes of the potential difference between cadmium or zinc and the solution, and these values will seem to change with the negative ion.

These normal cases are thus the ones in which no effect of the anion is to be observed. If we consider cells made up of metals standing in the electro-chemical series between magnesium and copper we have no change of the electromtive force with the change of the negative ion of the salt used in the solution, and with these metals there is little or no tendency to form complex salts. The metals following copper show a stronger tendency to form complex salts, and when there is such a tendency the electromotive force will be found to vary from the normal.

In view of these facts, I think that we may safely say that whenever the electromotive force of a cell appears to vary with a change of the negative ion the variation is really due to the formation of complex salts. With platinum and mercury the tendency to form complex salts is well known. That cuprous salts have this tendency, I think has not been observed, although such a tendency would be probable, as it occurs in all the metals to which copper is related. Cadmium also forms complex salts, and a slight current was observed to flow in the cell Cd | KI | KCl | Cd, thus explaining the reason that Hg | KI | KCl | Hg has a value slightly larger than the difference between the two cells Cd | KCl | Hg and Cd | KI | Hg. In both of these two liquid cells it is possible that we should obtain somewhat lower values; for the iodide solutions have a tendency to give too low readings. It will be remembered that iodide and chloride solutions behave somewhat differently, and with these two liquid cells it is impossible to be absolutely sure that at both electrodes the maximum constant potential obtains. If any error is introduced, it would be one in the direction to make the readings too high.

To determine the effect of the concentration, measurements were made with single liquid cells, reversible in respect to the anode. The results are given in Table XI, mercury being always cathode.

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[1] Zeit. phys. Chem. 16, 667 (1895).

TABLE XI.

$CuSO_4$	*n*	*n*/10	*n*/20	*n*/100	*n*/1000
	0.278	0.303	0.309	0.333	0.250
$CdSO_4$	*n*/10	*n*/1000	$CdCl_2$	*n*/20	*n*/1000
	1.041	0.975		0.814	0.900

The behavior of the various cells was very different. The normal copper sulphate cell gave its maximum reading at first, and at once dropped three to five millivolts, remaining constant for fifteen to thirty minutes. This constant reading was taken. The tenth normal cell slowly increased in value for about twenty-four hours and then remained nearly constant for several days. The hundredth normal cell reached its maximum in about six hours and remained fairly constant, but there was a certain tendency to polarize. With the thousandth normal cell, the tendency to polarize was very great and no readings of value could be obtained. It approached about 0.25 volts as a maximum, but even during a measurement it would rapidly fall to about 0.22 volts. The only thing sure about the cell is that it gives lower values than the other copper sulphate cells, The cadmium sulphate cells were very easy to measure, for the maximum reading was obtained in an hour or less and remained constant for several hours. The thousandth normal cell came to equilibrium very quickly and also polarized more readily than the tenth-normal. The value for the thousandth-normal cadmium chloride is not much more than an approximation. The cell increased slowly in value for a long time and no very definite maximum was reached.

For the the two liquid reversible cells the formula of Nernst is[1]

$$E = \frac{RT}{n_e}\left(\log\frac{P}{P_2} + \log\frac{p_2}{p_1}\right) \times 10^{-4} \text{ volts}$$

If p_2, the osmotic pressure of the ions of the cathode which have gone into the solution, remains constant, then for bivalent metals the electromotive force would increase 0.029 volts in pressing from a tenth normal to a hundreth normal solution of a salt of the anode metal. It would however seem that the concentration of the ions

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[1] Assuming that the two cations have the same migration velocity.

which have gone into solution from the cathode is a function of the concentration of the electrolyte used in the cell. In some of the cases, the variation is about what we would expect if p_1 were constant.

Some measurements were made with the cell $Cd|KCl+Hg_2Cl_2|Hg$, varying the concentration of the potassium chloride, with the following results: with *n*/10 KCl, 0.830 volts; with *n*/100 KCl, 0.910 volts; with *n*/1000 KCl 0.922 volts.

Except in the last case the values obtained were not at all satisfactory, and may be incorrect by as large an error as 0.025 volts. Each cell, however, a day or two after being set up reached a value which remained constant within a few millivolts for several days. The cells became alkaline and a very peculiar floculent precipitate formed on the cadmium. The correct values for the cells were thus rendered very uncertain, and the only thing to be observed is that the electromotive force varies with the concentration.

It will further be noticed that it was simply an accident that the cells containing a twentieth normal solution of a salt of the anode in several cases gave values so closely agreeing with the corresponding cells containing potassium salts; and therefore the hypothesis that the single potential differences are equal is erroneous.

In conclusion we shall consider the several important questions which have arisen. Do the one liquid non-reversible cells have a definite electromotive force? May they be considered as limiting cases of the reversible cells? What is the effect of the negative ion? If the electromotive force of these cells depends upon the ion concentrations caused by the air dissolved in the electrolyte there is no reason why we should not get a constant value. If the action of oxygen on the metals has any definite value, the term p_2/p_1 would be constant; for p_2 and p_1 would have the same relative value regardless of the amount of oxygen, at least within certain limits. The usual statement that these cells have no definite value because they depend upon the amount of air dissolved would seem to be entirely unjustifiable, and further the measurements of Bancroft and of myself show that these cells do have a perfectly definite value.

If the action of oxygen on the metals causing them to go into solution explains the reason why these cells have any electromotive force, then it would seem unjustifiable to consider them as limiting cases of the reversible cells where $p_1=p_2$, as will be seen from the following considerations. If the ratio of p_1 to p_2 is as small as 1 to 1,000,000 we should have only a variation of 0.174 volts from the cell where $p_1=p_2$. The value of the cell depends chiefly upon the term $\log P_1/P_2$. If the action of the oxygen on the two electrode metals is at all the same, we should find that the irreversible cells approach more or less nearly in value the reversible cells above mentioned. An approximate agreement between these two types of cells does not therefore prove that the irreversible cells might theoretically be considered as limiting cases of the reversible two liquid cells where $p_1=p_2$. Nothing short of a very accurate agreement would point to this, and we have no reason to suppose that the action of oxygen on two different metals would be the same, that is, that $p_1=p_2$. On the other hand it seems that these cells do not depend upon the oxygen dissolved for their value, since a cell made up of a potassium chloride solution containing a considerable quantity of pyrogallic acid with cadmium and mercury electrodes had a perfectly definite electromotive force of about 0.725 volts. In this solution there could, surely, have been no oxygen. If we consider $\log P/p$ as an expression holding strictly mathematically and $\log P$ as representing merely the tendency of the metal to go into solution, then this cell should have zero electromotive force. We may however look upon $\log P$ differently. If we immerse a metal in any given solvent we may suppose a certain small amount of the metal to go into solution till a certain equilibrium is reached between the solid metal and the metal in solution. We may then consider $\log P$ as representing the potential difference between the metal and the solution. This state of equilibrium we may safely assume is reached very quickly for we find that any one of the cells under consideration has, at the moment it is set up,an electromotive force not very different from its final value. If this is the case, we should always find the same potential difference between a given metal and a given solvent regardless of the electrolyte, provided that it is not a salt of the metal or cannot form a complex salt with the metal ions. If there is a possibility of the formation of a complex salt, the number of metal ions present will be depressed and the electromotive force correspondingly changed. According to this view it will easily be seen that these cells may be considered as limiting cases of the reversible cells, providing that no disturbing influence comes in.

If the single potential differences are really those found with dropping mercury electrodes there is a large potential difference between salt solutions and *log P*, the solution pressure of a metal, varies with the nature of the negative ion. Admitting this large potential difference between liquids would discredit the work of Neumann on single potential differences, which however agrees with the results of Le Blanc obtained by an entirely different method. Rothmund, Gouy and Luggin found, on measuring single potential differences by means of the change of the surface tension of mercury, that an error might be introduced in some cases where there was the possibility of the formation of complex mercury salts. If dropping mercury electrodes do not always give correct results, the solution pressure of a metal is independent of the nature of the negative ion. In every case where the electromotive force of a cell has been noticed to vary apparently with the negative ion, the possibility of complex salts is present. Cadmium forms complex salts, and we noticed a very slight current in the cell Cd | KI | KCl | Cd. The effect is very much larger with copper, mercury and platinum. Silver, gold, palladium, etc., all form complex salts with the halogens and would probably have the same behavior in a cell as mercury.

From this paper two principal conclusions may be drawn.

1. The potential difference between a metal and an electrolyte is not a function of the negative ion of the salt solution.
2. In certain cases dropping-mercury electrodes do not give correct values for the single potential differences measured by that method.

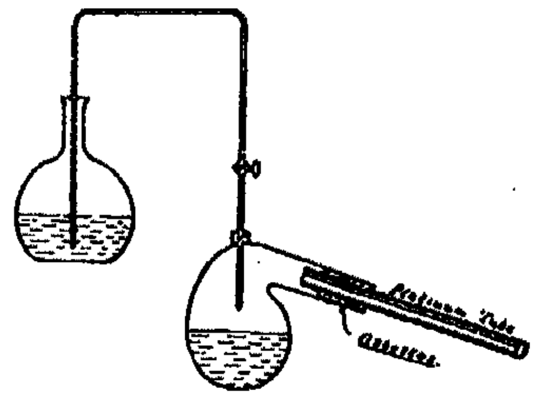
Cornell University, June, 1896.

PURIFICATION OF WATER BY DISTILLATION.

BY G. A. HULETT.

Ordinary distilled water suffices for almost all analytical purposes, but for atomic-weight work and many operations in physics water of a higher degree of purity is required. There seems to be little definite information as to apparatus and methods. Stas distilled his water from an alkaline solution of potassium permanganate after rejecting 1/20th, but still found ammonia. After distilling from potassium bisulphate and condensing in a platinum condenser he found it wholly free from organic and mineral matter. Kohlrausch[1] in preparing pure water, used potassium permanganate, potassium hydroxide and potassium bisulphate, in order to get rid of organic matter, volatile acids and ammonia; while Nernst[2] suggests purifying water by recrystallization.

In the present investigation the apparatus used possesses some points of advantage over that ordinarily employed. The condenser is a platinum tube 19 mm. in diameter, and about 60 cm. long. At the lower end the tube is contracted to 5 mm. diameter, and bent so as to pass into the neck of the receiving flask, thus preventing the distillate from coming in contact with the air about the still. This platinum condenser is provided with a short glass cooler, leaving about 20 cm. of the upper end free. About 15 cm. of this free end extends into the neck of a 4-liter retort, and the space between the platinum and glass is packed with asbestos. By this arrangement *only the water which is condensed in the platinum tube is collected*, while the water which condenses in the neck of the retort drips out at the asbestos packing.



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[1] Pogg. Ann. Erg. Bd. 8, 4 (1878.)

[2] Zeit. phys. Chem. 8, 120 (1891).

When there were more than two liters of the liquid to distill, it was found convenient to siphon water into the retort as fast as distilled. If it was necessary to reject the first portion of the distillate the larger portion, in a glass flask, can be boiled the desired length of time before the siphon is started. With this arrangement it is possible to distill large quantities of water and the apparatus needs no attention for hours at a time.

The most simple and delicate test for the purity of water is its electrical conductivity which can be determined by the method employed by Kohlrausch. The resistance cell was of the single bottle form, and the electrodes were each 25 sq. cm. and were not platinized. They were arranged in the form of concentric cylinders three mm. apart, and held in place by little pieces of glass fused to the lower ends. The resistance capacity of this cell was determined by comparing it with another of known resistsnce capacity, and also by using a 1/1000th normal sodium-chloride solution. Its value was found to be 1148×10^{-10}. Repeated determination showed an experimental error of 0.5 per cent. This cell gave a very sharp telephone minimum when used with the best distilled water.

VALUES OF $K \times 10^{10}$.

I	II	III	IV	V
10.8	3.75	3.01	4.44	1.17
6.78	4.11	1.40	1.67	31.0
4.85	1.58	0.88	0.99	102.0
3.68	1.25	0.76	0.79	3.01
4.03	0.77	0.76	0.80	2.90
3.20	0.96		0.80	3.93
2.93	0.76	0.76	0.79	47.9
			0.76	
		0.72	0.77	6.80
2.20	0.76		0.76	
		0.71	0.76	
	0.76	0.71		22.10
1.63		0.72	0.76	
	0.74	0.72	0.77	
1.46				
		0.76		
1.40	0.87			
1.47		0.87	0.78	

In general two liters of the water to be investigated were put into the retort, and the distillate collected in 100 cc. flasks, so that successive portions of the distillate could be tested. The first water investigated was from a surface well and an analysis by Mr. McLauchlan showed it to be unfit for drinking purposes. Two liters of this water were distilled, and the successive hundred cubic centimeters of the distillate gave the conductivities indicated in column I, of the table.[1] It appeared that after one-fourth had been distilled over, the remainder was quite good water. Following this suggestion and using the continuous distillation, fifteen liters of water were obtained with a conductivity $K \times 10^{10} = 3.3$. This water was then made distinctly purple with potassium permanganate, and after standing two days, was acidulated with 75 cc. sulphuric acid and carefully redistilled. Finally 2000 cc. were treated with 50 cc. of a saturated solutiion of barium hydroxide, and again distilled. The conductivities for the successive portions of this final distillate are shown in column II.

It is to be observed that the conductivity of the successive portions[1] of the distillate decreases rapidly, and after about a quarter of the water has been distilled, it reaches the value $K \times 10^{10} = 0.77$, where it remains practically constant during the remainder of the distillation.[2] It is to be further observed that the distillation may be continued without affecting the quality of the distillate until only about 100 cc. of the liquid are left in the retort.

A second series of observations was made, starting with the distilled water regularly used in the laboratory, Ten liters of this water, mixed with 50 cc. of a saturated solution of potassium bichromate and 50 cc. of sulphuric acid, were allowed to stand several days and then distilled. (The acid solution of potassium bichromate is a much stronger oxidizing agent than potassium permanganate, and seems to boil with less bumping.) Two liters of the distillate were distilled with 50 cc. of the barium hydroxide solution. The results are shown in column III of the table,[3] and are in close agreement with those in No. II. It thus appears that the methods here

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[1] It took from 8 to 9 minutes to distill off each portion.

[2] The time of the distillation was 6 to 8 minutes per portion.

[3] Each portion distilled in about ten minutes.

described yield distilled water which leaves nothing to be desired as far as any impurity affecting the conductivity is concerned. It needs to be added that repeated distillation of this final distillate did not lead to any noticeable reduction of the conductivity below 0.76. Kohlrausch concludes from his research that the best water distilled in the air has a conductivity of 0.70.

Barium hydroxide is a strong base and seems to be an admirable reagent for retaining the carbon dioxide and volatile acids. The results show no indication of barium hydroxide having been mechanically carried over during the distillation. To test this point further, two liters of the best water with 50 cc. of the solution of barium hydroxide were distilled at a slow rate[2] until the distillate showed a conductivity $K \times 10^{10} = 0.76$., and then the rate of distillation was gradually increased until it was 17 cc. per minute. The results are found in column IV. Comparing these results with those in I and II, it apears that *the quality of the water is independent of the rate of distillation* when barium hydroxide is employed to fix the acids. The last 100 cc. gave a conductivity of $K \times 10^{10} = 0.87$, leaving only 55 cc. in the retort ! With sulphuric acid, however, the case is altogether different, as appears from the following series of observations : Two liters of water, conductivity $K \times 10^{10} = 0.80$, and 50 cc. of sulphuric acid were slowly distilled. All portions of the distillate gave high conductivities, as shown in column V. A portion of the distillate was concentrated and, when tested with barium chloride, showed sulphuric acid. An inspection of these irregular results suggests that some of the liquid in the retort was mechanically carried over, but as all portions of the distillate show a conductivity much above that of the water employed (0.80) it raises the question whether some sulphuric acid does not *distill* over with the water.

In order to test the quality of water to be had by the method of continuous distillation five liters of the distillate, from potassium bichromate and sulphuric acid, were divided between the retort, and a 3-liter glass flask from which it could be slowly siphoned. After redistilling and rejecting the first 400 cc., during which time the water in the flask was also boiled, the siphon was started and two liters of the distillate collected. The sample showed $K \times 10^{10} = 0.87$

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[2] 12–24 minutes for each of the first eight portions.

The next liter gave 0.78. Then successive portions of 100 cc. gave respectively: 0.76, 0.80 and 0.87, leaving but 100 cc. in the retort. It is possible that a tin tube of the same construction would answer for water. According to A. C. McGregory[1], a condenser of good glass answers every purpose.

In conclusion, I wish to express my thanks to Dr. E. H. Loomis for many suggestions and kindly interest in the above work.

Princeton Chemical Laboratory, June, 1896.

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[1] Inaugural Dissertation, Strassburg, 1893.

NEW BOOKS.

Die modernen Theorien der Chemie. Buch I: Die Atome und ihre Eigenschaften. *Lothar Meyer. Sixth Edition. Large octavo. xviii and 171 pages. Maruschke und Berendt. Breslau. 1896. Price 5.60 marks.* In preparing a sixth edition of his well known book «The Modern Theories of Chemistry», Lothar Meyer decided to publish the work in three separate volumes, corresponding to the three parts into which the previous edition had been divided. The present volume forms the *first part* of the new edition . . . the continuation of the work is prevented by the untimely death of its author.

The first part is modelled closely on the corresponding sections of the last edition, which has enjoyed such a wide circulation, in English as well as in German, that a closer description is unnecessary : it is sufficient to note that the book has been brought up to date by a thorough revision of the experimental data, and admission of the results obtained since 1888. The additions are especially noticeable in the tables; in that of the vapor density of the elements, for example, fluorine appears for the first time, while to the table of the vapor densities of compounds, derivatives of five elements are added ; the paragraph on the vapor density of acetic acid is supplemented by an account of those of the chlorides of aluminum and other metals ; and in the chapter on the periodic law, a section has been devoted to the positions of germanium and argon. Similarly throughout the work ; the curve of atomic volumes, at the close, has been revised to correspond with the text. To make room for the numerous additions, the discussion of some of the results has been much shortened, the account of the optical properties as a function of the atomic weight reserved for a subsequent volume, and some of the less successful hypotheses, *e. g.* the author's «particle» theory, and Pictet's rule for calculating melting-points—have been omitted altogether.

In view of the many notable improvements in the book, the retention of 15.96 as the atomic weight of oxygen is a little surprising; it is perhaps owing to the circumstance that the preface is not completed, that no explanation has been given of the retention of a number which seems much less likely to remain permanently in use than either the more accurate 15.88 or the arbitrary—and convenient—16.00.

There is one other point which must not be passed over in the review of a work which everywhere exercises so great an influence on the teaching of chemistry. Throughout the book—in the preface, in the introduction, in the body of the work, and in the conclusion,—may be found repeated warnings *not to confuse facts with hypotheses:* but is not the effect of these exhortations on the mind of the reader liable to be seriously impaired, in one important point at all events, by the very mode of treatment of the chemical theories adopted in this book? To entitle the work itself: «The Atoms and their Properties», and its first chapter: «The Necessity of the Atomic Hypothesis»—is not this to blind the student to the fact, that, after all, the subject matter of the volume in question is but the vapor densities, specific heats and laws of combination, *not* of atoms, but of matter in quantity—is but the results of quantitative experiments, which may, and in the future most probably will, be looked at from another point of view than that of the atomistic theories of to-day?

Taken as it stands, though part of an unfinished book, the volume forms a complete and useful monograph on that part of the theory usually treated of in the elementary lectures on chemistry; and its publication in a separate form will make it more useful than ever—because more accessible—to students of that subject.

W. Lash Miller.

Grundzüge der Eektrochemie, auf experimenteller Basis. *R. Lüpke. Second Edition. xi and 186 pages. Julius Springer. Berlin. 1896. Price 2.60 marks.* This book begins with a description of the phenomena of electrolysis, which leads up to experiments illustrating Faraday's law, and Hittorf's conception of the relative velocities of the ions; an account of Kohlrausch's work on the conductivity of dilute solutions, and of Arrhenius' theory of electrolytic dissociation in which Kohlrausch's results received their molecular-theoretical interpretation, bring the first section of the work to a close.

The next part (pages 58–59) is devoted to van 't Hoff's theory of solution. Beginning with an account of the classic experiments of Pfeffer on osmosis, the author passes to a description of methods for accurately determining the vapor tension, boiling point, and freezing point of solutions, formulates the general laws of these phenomena and the exceptions met with in the case of electrolytes, and finally shows the quantitative connection between all these branches of physics, in the light of the modern theory of solutions.

The third section entitled «The osmotic theory of the current in voltaic cells», opens with an abstract of Nernst's celebrated paper in which was made the first application of the osmotic pressure theory to the calculation of E.M.F. The use of the formulæ deduced in this article is illustrated by chapters on concentration cells, Daniell's cells, and cells involving oxidation and reduction; while the next two chapters, on «solution tension of the metals» and on «polarization» respectively, close this part of the subject. A chapter on irreversible cells, one on storage batteries and ten pages on «the energetics of the galvanic element» complete the book.

Lüpke's «Electrochemie» is intended for the use of the «ordinary» chemist who wishes to learn something of the recent rapid progress in this branch of his science, and the author has endeavored to give him as clear an idea as possible, both of the discoveries themselves and of the theories based upon them, by describing a large number of carefully selected experiments, and by restricting the use of the mathematics to what is absolutely necessary ;—as is usual in works of this nature the element of criticism is almost entirely wanting.

Thoroughly in accord with the object of the work is the introduction of the long article (41 pages), on the theory of solutions. In this section however there may be noticed a certain, almost polemical, tone, which was surely more in place at the time when the theories in question were first being introduced, than it is at the present day when their usefulness has been abundantly demonstrated, and when those who «do not believe in ions», *i. e.* who do not understand how to make use of this new tool of quantitative research, are merely those who have no knowledge of the great advance made during the past ten years in the study of chemical and electrical phenomena.

In contrast with this full treatment of the osmotic theory is the scant attention paid the theory of energy ; no attempt has been made to emphasize the important point, that it is only owing to the «reversibility» of the cells discussed in chapters 1 to 4, section III, that any calculation of their E.M.F. can be made ; and, more excusably perhaps, the account of the influence of the temperature on electrochemical reactions is based on equations for which no deduction is given.

On the whole, the author must be regarded as eminently successful in his attempt to make clear the conceptions and theories introduced in the development of this important subject ; the work may be heartily recommended, not only to the class for which it is designed, but also to teachers of the subject, who will find in the little volume a surprisingly good collection of instructive experiments for use in the lecture room and in the laboratory.

W. Lash Miller.

The Practical Methods of Organic Chemistry. *Ludwig Gattermann, Ph.D. a.o. professor in the University of Heidelberg. Authorized translation by W. B. Shober, Ph.D., instructor in organic chemistry in the Lehigh University. XII and 329 pages. The Macmillan Company, New York. 1896. Price $1.60.* Professor Gattermann's book differs from those previously published on the same subject, in possessing a «general part» of 104 pages dealing with the operations of crystallization, sublimation, distillation, etc., with the determination of melting and boiling points, the correction of the thermometer and the methods of qualitative and quantitative organic analysis. Considering that V. Meyer was one of the very first to apply the newer methods of molecular weight determination to the solution of problems in organic chemistry, it certainly cannot be from a want of appreciation of the value of these methods that, in a book issuing from his laboratory, no instructions are given for carrying them out. It is much more likely that the author expects every student to be provided with one of the numerous manuals recently published on this subject ; still a few pages on the determination of molecular weights, by freezing point and boiling point estimations for instance, would have added greatly to the value of the «general part.» In the «special part» the preparations selected are grouped under general heads with a view to showing their value as types: a year's experience with the book in the laboratory has convinced the reviewer that in this respect also the work is a decided advance on those of Levy and Fischer.

The present translation is «intended for those students of chemistry who have not yet become sufficiently familiar with scientific German to read it accurately without constant reference to a dictionary»—but can there be any doubt that the best way to help such students over their difficulty is to let them use the German original?

W. Lash Miller.

Grundriss der physikalischen Krystallographie. *Th. Liebisch. Large octavo, viii and 506 pages. Veit und Comp. Leipzig. 1896. Price 13.40 marks.* This work affords a more straightforward introduction to the theory of the thermal, magnetic, electric, optic and elastic properties of crystals than any other book the writer knows. The chapter on geometric crystallography is not so effective as it would be if the author had arranged to give greater typographical prominence to the scheme of classification.

In any geometric discussion it is primarily important to so bring out the relations to be established as to enable them to be *perceived.* The writer is decidedly of the opinion that the application of algebraic analysis to such discussions must tend to grow less and less frequent in the development of theory and to become more and more restricted to the degradation of complex geometric relations to scalar schemes for the purpose of numerical calculation. As an example one may cite the derivation of the law of rational indices from the law of zones. The identity of these two laws can be perceived directly by one who has even a little geometric imagination, and being once perceived one can write down at a stroke, as it were, all the equations which have to do with the matter. Geometric conceptions being once grasped in any physical problem, scalar equations can be written down *ad libitum* when needed—and this is only when one is going to make measurements and reduce them, that is when one is going to *use* the equations. This is what the promoters of vector analysis have in mind, except in so far as they are enamored of various elegancies or fabrications that are useless, as for example many of the developments of quatermions! If the writer were to offer advice it would be that students of physics and especially of chemistry, for these are wofully lacking, should study geometry ; if required to give further advice to chemists it would be—study crystallography! and if urged further he would, without essential hesitation, add—study as a beginning Liebisch's *Grundriss der physikalischen Krystallographie*.

Chemists have hitherto largely confined themselves to the operations of *mixing* and of *separating*—physicists indeed stand astonished at what they have accomplished by that—but physical chemistry, properly so called, is the *Idea* of the bringing to bear of detailed study of the physical properties of *phase material* upon the questions which have hitherto been the objects of the chemist's scrutiny. Who can set limits to his expectancy of knowledge who, not content with the mere fact that *this* stuff separates from *that* mixed stuff when it is squeezed and cooled, proceeds to investigate and classify the numerous physical properties of various stuffs!—a complex problem, indeed, this of classification ; but then as reassurance we need only remember that we know a great deal about electricity and magnetism, for example, because it *is* complex, and very little about gravitation because it is so elusively simple!

W. S. Franklin.

Lehrbuch der Chemie. Band I: Anorganische Chemie. *G. Bodländer. large octavo. xvi and 660 pages. Ferdinand Enke. Stuttgart. 1896.* Those who have followed the active development of physical chemistry in recent years will greet with pleasure an effort to introduce the results of this work into an elementary text book on general inorganic chemistry. The need for such an attempt has become more and more deeply felt for some time. In the plan of our present author, who has undertaken the task, a necessary basis of chemical facts is obtained at the outset through a study of a few typical elements and their more important compounds. The choice is the usual one: the fixed gases and carbon, with their simpler compounds. Molecular formulas are then introduced as simple expressions of the laws of simple and multiple proportions and of the volume-combination law of Gay-Lussac. The atomic and molecular hypotheses are added later, and the whole general introduction is concluded by an outline of the theory of solutions, the valence theory and the hypothesis of electrolytic dissociation. The appearance of this last before many salts have been studied seems premature.

The body of the book is broken into two parts, dealing systematically with the non-metals and the metals respectively. Attention is here directed chiefly to those substances and reactions which have a practical interest by reason of the use made of them in analysis, in medicine or in the arts. An especially interesting feature is a chapter on thermochemistry, placed very suitably near the close of the «book» on non-metals. Under the head Carbon an extended chapter of over fifty octavo pages supplies a general review of the field of organic chemistry, for the information of those chemists «who have no opportunity to busy themselves with organic chemistry». This object will not excite universal sympathy, and the treatment is so extended as to seem thoroughly out of place. At the beginning of the third «book», on metals, is a pleasing account of electrochemical matters, where electrolysis, electrical energy and electromotive forces, and the ion theory of chemical reactions are introduced. Accumulators are taken up later under the special heading of Lead.

The descriptive chemistry of the book is excellent. Yet to set out with oxygen and combustion would seem to some more natural than to begin with hydrogen as the author has done. Much physical chemistry of a simple kind is to be learned from the text; but the entire omission of the phase rule is a woful neglect, for the subject of inorganic chemistry is certainly the one department at the present time where the phase rule bears most. Regarding the physical chemistry of the book it may be said that the derivation of the formula for the reduction of gas-volumes to standard conditions, on page 9, is not clear; the law of mass action is treated simply and well; the discussion of the solution theory and of electrolytic dissociation is commendable. The chapters on thermochemistry and on electrochemistry contain also much that is good. In the former we find besides the usual topics a few pages on energy and its factors, but *work* and *energy* are here discussed without the meaning of these terms being made definite and it is not made clear why one particular quantity instead of some other is pitched upon as an «intensity» or a «capacity» factor in any given case. The whole matter is so confused and misleading that it would have been better to have omitted it altogether. Other examples of the kind are the assertion under Electrochemistry that

Electrical energy=colulombs × *volts,*

and the remark that in the inversion of cane sugar the quantity

$$\frac{1}{t} \log_e \frac{a}{a-x}$$

—where of the initial sugar a the portion x is inverted at the time t—«remains constant for all values of t, a result which is a simple consequence of the law of mass action». Blank statements of this kind are of no use, such results as the above should be stated intelligibly or not at all. Existing elementary treatises on chemistry suffer severely from this sort of thing.

Notwithstanding the above objections the book before us is on the whole a very good one. It contains rather too much material to be read profitably by the beginning student, but it can be used with great advantage to supplement a briefer introductory course—and every serious student of chemistry should round out his initial course with the help of some work of this kind.

J. E. Trevor.

Lehrbuch der Experimental-Physik. *Eduard Riecke. Large 8vo. Vol. I 418 pp, Vol. II 492 pp. Veit und Comp. Leipzig, 1896. Price, Vol. I, 8 marks; vol. II, 10 marks.* The present work is a text book, in two moderate volumes, on general physics, and since it is intended to be «easy to read» it involves but slight employment of mathematics. The first volume is concerned with Mechanics (including Sound) and Light. We note particularly in the Mechanics a chapter on Energetics—where the waste of work in the production of heating effects is introduced—and very interesting text on the physical behavior of gases and on currents and vortices in fluids. Under the title Molecular Phenomena the term *molecular action* is defined as a name for actions which appear only upon the contact of bodies. The author here, page 179, writes :—«The assumption of molecular constitution and of forces acting among molecules . . . contains a series of arbitrary assumptions whose justification is in no wise securely founded . . . and may not be dogmatically regarded as a demonstrated matter. It is therefore desirable to assemble the groups of molecular phenomena under yet another, more general, point of view. Such an one appears in the consideration of the forms of energy underlying them.» This is interesting, and praiseworthy as far as it goes; the subjects treated are elasticity, capillarity, osmotic pressure and gas-theory. The remainder of the volume is occupied by Sound and Light.

Magnetism and Electricity (considered together), with Heat, constitute the subject matter of the second volume. Galvanism as presented here comprises chiefly Ohm's law, the Hall phenomenon and the law of Joule. The «book» upon Electrochemistry supplies a simple and fairly comprehensive exposition of electrolysis, electrolytic dissociation and electromotive forces. A compactly put study of thermoelectricity too has physicochemical interest. Enterprise in the selection of material is indicated by the somewhat unusual treatment of lightning discharges, and the researches of Hittorf, Crookes, Lenard and Roentgen upon cathode rays. Nearly two pages also are devoted to Tesla.

The chapters on Heat contain much more of physical chemistry than is usual in elementary books on physics, Gibbs's criteria of thermodynamic equilibrium are for example included in the introductory chapters on thermodynamics. Under the title Changes of State the processes of fusion and of vaporization are clearly treated; the theory of the thermodynamic potential is outlined and applied to simple monovariant boundary curves; the phase rule is derived and illustrated with the system sulfur dioxid and water, and these matters are followed in order by the theory of dissociation, the physical theory of solutions and the equation of van der Waals. The remainder of the volume describes Conduction and Radiation. An exhaustive index completes the whole. The illustrations are good and the book is well printed, it may on the whole be fairly regarded as the representative of an interesting course of elementary lectures on experimental physics.

J. E. Trevor.

The Elements of Physics. Volume I: Mechanics and Heat. *E. L. Nichols and W. S. Franklin. xi and 228 pages. Macmillan and Co., New York. 1896.* In their new text book on Physics Nichols and Franklin have undertaken to supply a concise statement of laws and a systematic development of principles, to accompany and supplement experimental lectures or laboratory demonstrations for students beginning physics. In carrying out this plan the worst of the customary difficulties of presentation have been entirely avoided through the frank use of a little calculus, with the natural result that the treatment so secured is clear, concise and in every way intelligible and agreeable. The work is to appear in three small volumes, the first of which, now before us, treats Mechanics and Heat. The Mechanics sets out with the measurement of length, angle, area, mass and time, together with an admirable disquisition upon units, vectors and variable quantities; which introduction is then followed successively by chapters on the laws of motion, on statics, energy, moment of inertia, elasticity, friction and hydromechanics. The remainder of the volume, a full third of the whole, is devoted to Chemical Physics and Heat. Under Chemical Physics appears brief comment upon the stoichiometric laws, crystallography, solubility and diffusion—considerable attention being devoted to the crystallography; while under Heat we find the usual subtopics,—thermometry, calorimetry, gas-laws and thermodynamics. The material presented has been carefully chosen throughout. The only omission of importance noted is that of the Gibbs Phase Rule, from the chapter on Chemical Physics.

Among the peculiar excellences of the volume, apart from the important one of its general plan, may be noted the full and clear treatment of vectors and that of harmonic motion, and perhaps also the introduction of the term *sweep* for an irreversible process—the word seems not badly chosen. It is on the other hand distressing to be told, page 151, that the theory of thermodynamics is based upon the «constancy of average behavior of molecules», that «the energy stored in a body by virtue of the state of its molecular motion is called heat», and much more of the like. It seems in fact to the reviewer that the dogmatic kineticism of the book is its one serious fault.

The proof reading has not been done with the care which one would expect in so important a book; the English of the text needs revision in a few places and there are such errors as «single» for simple (page 37), «names» for masses (page 39) and «incomprehensible» for incompressible (page 112). As minor flaws may be mentioned also the employment of *angular velocity* on page 6 before its definition on pages 46 and 55, and a note on page 185 where Gay-Lussac's volume-combination law is attributed to Berzelius. That Chemical Physics appears as a chapter of Mechanics is perhaps not to be objected to. The general style, however, of the book is admirable; it is well planned, well arranged, and is well illustrated with new and very helpful drawings. The student who reads it through attentively will certainly learn considerable physics.

J. E. Trevor.

Miscellaneous Papers. *Heinrich Hertz. With an Introduction by P. Lenard. xxvi and 340 pages. Macmillan and Co., Ltd. New York. 1896.* As a companion volume to the English version of Hertz's *Electric Waves* the Macmillan Company has recently issued a translation, by D. E. Jones and G. A. Schott, of the *Miscellaneous Papers* of the same author,—the first volume of the now well-known German editon of Hertz's collected works. We note with pleasure that a translation of the concluding volume, the *Principles of Mechanics*, is announced by the same publishers.

Of particular interest here to the physical chemist are the important papers on evaporation and on the vapor pressures of mercury, reprinted from Wiedeman's Annalen, the article on Helmholtz and, for its thermodynamic bearing, a delightful paper on the adiabatic changes of moist air. The papers on the cathode rays will doubtless also fall into this same category before long, and the popular address on the relations between light and electricity (1889) is of general interest to everybody. It seems likewise probable that Hertz's exact theoretical formulation of the property of *hardness* will become fundamental for the future determination of relations subsisting between hardness and chemical composition and constitution, the author's comments (Introduction, page *xix*) upon his work on this subject are charming. The book is prefaced by a biographical introdution written by Lenard of Bonn, containing many extracts from Hertz's letters about his scientific work. A handsome portrait, engraved especially for the volume, has been added as frontispiece.

The collection has been treated as a classic should be. Translated exceedingly. well and printed handsomely with large type on heavy, highly finished paper the execution leaves little to be desired; the volume forms a handsome as well as a very important addition to one's book-shelves. *J. E. Trevor.*

Studien zur chemischen Dynamik: *Nach J. H. van't Hoff's Études de Dynamique chimique. Bearbeitet von E. Cohen. Mit einem Vorwort von J. H. van 't Hoff. Large octavo. vi. and 282 pages. W. Engelmann. Leipzig. 1896. Price 6 marks.* The object of this book is a twofold one. It is to serve as a reprint of the «*Études de Dynamique chimique*» and it also contains some of the later work done in the Amsterdam Laboratory, presented from the same point of view as far as may be. The new book takes up the subject in the same order and under the same headings as the old one; but each chapter is very much enlarged and often transformed. Among the noteworthy additions are the researches on the oxidation of phosphorus, sulfur and aldehyd; Noyes's application of the van 't Hoff principle for determining the order of the reaction; a mass of new data on the change of the equilibrium constant with the temperature; a large part of the chapter on condensed systems; a very satisfactory recapitulation of the methods of determining inversion temperatures; the calculation of the change of solubility with the temperature; additional data on the effect of pressure on condensed systems; the recent work on the tartrates and the discussion of Cohen's concentration cell. Ewan's work on the freezing points of sulfuric acid solutions is not included, while all of van 't Hoff's work on dilute and solid solutions is omitted.

While the book, taken as a whole, is most excellent and satisfactory there are a few details which seem open to criticism. It was necessary to say something about condensed systems for historical reasons; but it would have been much better to have supplemented this by showing the increased simplicity and completeness obtained by the application of the Phase Rule. It is very curious to see how little the work of Roozeboom has affected the point of view adopted in the Amsterdam Laboratory. The statement on page 171, that at the inversion temperature there is a complete change from one system to the other is true; but very misleading. The inversion temperature is really a limiting temperature for only one phase. On page 170 it seems a pity to find in two successive sentences: «Both systems can never exist simultaneously » and « both systems can occasionally exist simultaneously ».

The Reviewer wishes to protest most emphatically against the statement, page 149, that the Mass Law holds only for dilute solutions. In his opinion the Mass Law, when properly applied, is absolutely accurate and it is our only chance of escape from the tyranny of « ideal » solutions. The distinction between physical and chemical reactions does not seem to be a happy one. According to it, the transformation of rhombic into monoclinic sulfur is a physical change if the sulfur be vaporised, raised above 95° and then condensed, while it is a chemical change if the crystals pass from one form to the other.

The style is clear, though somewhat diffuse; the methods are described in such detail and there are so many illustrations that the book could be used as a Laboratory Manual. There are a few unimportant misprints on pages 25, 70, 184 and 236. A more serious one is the statement on page 175 that the double sodium and ammonium racemate changes into the single tartrates, when racemates are meant. The references are very complete but it is inexcusable not to give the year as well as the volume and page.

Wilder D. Bancroft.

Das Parallelogramm der Kräfte als Grundlage des periodischen Systems in der Chemie. *J. Sperber. 8vo. 37 pages. G. Speidel, Zürich. 1896. Price 1.50 marks.* The author deduces two important conclusions on the very first page in something the following manner: Since allotropic modifications may have different properties, all the so-called elements must be modifications of the same thing. Since two elements may have the same valence and one element two or more valences, there must be definite angular relations between atoms in a compound. As a consequence, the combining weight of carbon is 12.5. Realizing that a hypothesis must give quantitative numerical results to be accepted, the author calculates the heats of formation of the different halogen acids. Curiously enough, the value for hydrobromic acid, calculated on the assumption of bromin in the gaseous form, agrees very nearly with the experimental value for the same compound starting from the liquid bromin.

It is not this coincidence which the author looks upon as «an irrefragable proof of the accuracy of the periodic angle-system.»

Wilder D. Bancroft.

Handbuch der Elektrochemie. *F. B. Ahrens, large 8vo, 524 pp. Ferd. Enke, Stuttgart, 1896. Price 13 marks.* This book appeals to two classes of people, to students of electrochemistry who wish to learn something of technical methods and to technical students who are interested in electrolytic analysis. The book opens with a discussion of the sources of electrical energy, including under this head, standard and normal cells, thermopiles, dynamos and accumulators. Then comes a short chapter on electrical units and a very complete one on methods of determining the same. Four pages are given up to a thoroughly unsatisfactory discussion of electrical energy and heat effect and of galvanic polarisation. A brief review of the theory of the voltaic cell and a chapter on switches and commutators brings us to the end of the first part. In the second part there is a very complete account of the analyses and syntheses which are effected by electrolytic methods. The book is profusely illustrated and describes very fully the various ways in which different factories attain certain results. This feature is the one which will probably be of the most value to readers.

The book is distinctly a compilation of facts. The author adds nothing of his own and makes no attempt to show why certain conditions are more favorable for a good yield than any others. It is sufficient for him to chronicle the results of experiments without trying to find what scientific principles underlie them. Wherever it is impossible to avoid stating theoretical results the author gets into difficulties. It is no longer customary to speak, as on page 13, of zinc changing to zinc oxid and the latter dissolving in sulfuric acid. The equation of Helmholtz was not tested by Braun and Jahn, page 116, but by Czapski, Gockel and Jahn. Braun's work preceded that of Helmholtz and was carried on at a constant temperature. It will surprise Kohlrausch to learn, page 166, that he has proved pure water to be an absolute non-conductor. It is a very unusual way of describing the electrolysis of sulfuric acid to say that the unstable compound SO_4, breaks up into oxygen and sulfur trioxid, the latter combining with water to regenerate sulfuric acid. The historical development of the dissociation theory, page 168, will hardly be recognized by those who took part in it. The calculation of the electromotive forces necessary to decompose different salts, pages 246–253, is not to be taken seriously, and there is no authority for the statement, page 284, that the hydrate $H_2SO_4\frac{1}{2}H_2O$ is decomposed by the current.

Wilder D. Bancroft.

Les nouvelles théories chimiques. *A. Étard. 196 pages. Gauthier-Villars et Fils. Paris. 1896.* This little volume is devoted to an elementary discussion of the fundamental theoretical conceptions on which chemistry, as a science, rests, including the physical interpretation of many physical phenomena. Indeed the author considers general chemistry as a study of the physical properties of atoms and molecules. After general definitions of matter, conservation and transformations of energy, elements, compounds, *etc.*, the book deals with the atom, the molecule and the ion, giving in connection with the ion, a brief summary of the theory of Arrhenius. Under the chemical properties of the atoms and molecules, the laws of definite and multiple proportions, the substitution theory of Laurent and Dumas, homology and isomerism are briefly discussed. The following chapter on the gaseous state treats chiefly of the fundamental gas equation, the hypothesis of Avogadro, the law of Gay-Lussac, and the determination of vapor density—especially by the method of Victor Meyer.

In the chapter on the liquid state prominence is given to the theory of van der Waals, to osmotic pressure, and to some of the more familiar phenomena exhibited by solutions, such as the lowering of the vapor pressure and the lowering of the freezing-point of the solvent by the dissolved substance. Under solids, matter is discussed in its crystalline forms, chiefly from a morphological standpoint.

The second part of the work has to do with the general properties of the molecules, discussing, under the relation of mechanics to chemistry, the law of mass action and the velocity of reactions. Thermochemistry and electrochemistry are dealt with very briefly, while photochemistry is considered at somewhat greater length.

There are certain omissions in the book to which it is necessary to call attention. The reader would gain the idea that the Periodic Law was due to De Chancourtois and Mendelejew, while the very important suggestions of Newlands and Lothar Meyer are not considered. Again, the work of Julius Thomsen in thermochemistry, which is second in importance only to that of Berthelot, is omitted.

The book as a whole is, however, clear and unusually concise, and can be heartily commended.

Harry C. Jones.

REVIEWS.

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

General Theory and Thermodynamics.

Note on the Theorem of Clausius. *Edgar Buckingham. Phys. Rev.* 4, *39* (*1896*). The purpose of this note is to demonstrate the existence of the second law of thermodynamics, or the existence of an entropy function, for systems whose state is defined by more than two independent variables, of which the temperature shall be one. Where the system is completely defined by two such variables and where the work done by or on it is mechanical and hence of the form $\int pdv$, the existence of the Thomson absolute scale of temperature is assumed. This of course determines the existence of an entropy function for these conditions.

The author next shows where the work done by or on the system is not mechanical but is completely convertible in either direction with mechanical work, that the same laws must hold. To this end an agent or mechanism is assumed capable of thus converting the work in either direction. The system may then by means of this converter be coupled to a Carnot engine, and the efficiency of operation of the former will manifestly be that of the latter, and hence the entropy function will exist for the assumed system the same as though the work were entirely mechanical.

The author next takes up the general case by assuming a system whose state is defined by $(n+1)$ independent variables of which the temperature is one. These are denoted by $t\, c_1\, c_2\, c_3$, etc. These variables are to be so taken that variation of t alone shall not result in any external work. This restriction is shown not to affect the generality of the treatment. In order to obtain a continuous representation of the condition of such a system by means of the locus of a point we should require space of $(n+2)$ dimensions and the locus would be a geometrical concept of $(n+1)$ dimensions. The general treatment of the subject from this standpoint requires therefore the use of geometry of more than three dimensions, and is, in consequence, not suited to a simple or elementary presentation. The chief purpose of the author is to give a satisfactory treatment which shall avoid the use of hypergeometrical concepts.

The heat required in a cyclical process involving change of temperature alone will necessarily be zero. The variation of the other variables will result in the performance of work w, the element of which is expressed in the form :

$$dw = \frac{\partial w}{\partial c_1} dc_1 + \frac{\partial w}{\partial c_2} dc_2 + \dots$$

Suppose the system to vary through a cyclical process. The partial derivatives in the above equation will correspondingly vary. Let now n plane diagrams be plotted by laying off in each the value of the partial derivative as an ordinate on the value of c as an abscissa. For the cyclical process we shall have in general n closed diagrams, the area of each of which will represent the work done in connection with the variation of the corresponding variable, and the sum of these areas will therefore represent the total heat required. The attention is now fixed on these n diagrams and it is shown that if the system be carried through a series of changes alternately isothermal and adiabatic, the paths described on the diagrams will each be made up of isothermal and adiabatic pieces. It is then shown that each of these closed curves may be replaced by a broken path made up of isothermal and adiabatic steps, and that in this way the original cycle may be broken up into an infinite number of equivalent Carnot cycles, and *vice versa* that the sum of the latter must be equivalent to the former. For each of the Carnot cycles, as previously shown, we shall have :

$$\frac{Q_2}{T_2} - \frac{Q_1}{T_1} = 0$$

or

$$\int \frac{dQ}{T} = 0$$

The same result will hold also for their sum and hence for each of the closed paths, and hence for their sum, or for the entire cyclical variation of the system. Hence for such a system and on the basis assumed, the entropy function defined by :

$$d\eta=\frac{dQ}{T}$$

does exist.

The author also shows that the function η thus defined is necessarily of such character that its variation may be considered as completely determined by the variation of the defining variables of the system, and hence that we may take partial derivatives of η with reference to such variables.

The proof of this point is perhaps unnecessarily long, as it seems to follow directly from the fundamental assumptions expressed in the following equation :

$$dQ=\frac{\partial Q}{\partial t}dt+\frac{\partial Q}{\partial c}dc_1+\frac{\partial Q}{\partial c_2}dc_2+\dots\dots$$

hence $$\frac{dQ}{t}=d\eta=\frac{1}{t}\frac{\partial Q}{\partial t}dt+\frac{1}{t}\frac{\partial Q}{\partial c_1}dc_1+\frac{1}{t}\frac{\partial Q}{\partial c_2}dc_2+\dots\dots$$

The various terms on the right must by the form of the equation be considered as the partial derivatives of η, and we must have therefore :—

$$\frac{\partial\eta}{\partial t}=\frac{1}{t}\frac{\partial Q}{\partial t}$$

$$\frac{\partial\eta}{\partial c_1}=\frac{1}{t}\frac{\partial Q}{\partial c_1}\,.$$

It may be noted that in the treatment given by the author the assumption of the n plane diagrams does not seem to be an essential feature, although it is doubtless an aid to the perception, and these diagrams furnish a clear representation of the distribution of the work among the various factors involved in the change of the system. The fundamentally essential point of the treatment would seem to lie in the equation giving the value of ∂Q as written just above. The first term is concerned with internal energy alone and hence for a cyclical process is zero. The remaining terms are of the order of external work either mechanical or completely convertible in both directions with it. For each of these terms therefore the entropy function must exist, and hence for their sum and hence for any cyclical process we must have:

$$\int \frac{dQ}{T} = 0.$$

W. F. Durand.

Qualitative Equilibrium.

On the Characterization of optically Isomeric Compounds. *F. Walden. Ber. Chem. Ges. Berlin.* **29**, *1692* (*1896*). The comparison of a large number of substances leads to the following conclusions:

i. Crystallization in hemihedral forms is a usual but not necessary accompaniment of optical activity in solution.

ii. The electrolytic-dissociation constant *K* is the same for the *d.* the *l.* and the racemic modifications of acids.

iii. The *d* and *l* forms have the same density, solubilities and melting point.

iv. The melting point of the racemic form may be the same, higher, or lower than that of the *d* and *l* forms.

v. The form with the higher melting point has the smaller molecular volume and is less soluble.

vi. Any inactive compound prepared by the union of *d* and *l* forms has a right to the title «racemic» if its crystalline form and its density be different from those of the active components: in general the melting point and solubilities are also different.

W. L. M.

Remarks on the End-point in Titrating for Silver according to Gay-Lussac. *C. Hoitsema. Zeit. phys. Chem.* **20**, *272* (*1896*.) Since the solubility of silver chlorid is decreased by the presence of silver nitrate or of sodium chlorid, addition of either should produce a precipitation of silver chlorid indefinitely. Practically, the change in the solubility of silver chlorid, per drop of precipitating solution added, decreases so rapidly that it soon ceases to be visible. The influence of sodium chloride and of silver nitrate being the same, the mean of the points where a drop of each solution produces no perceptible precipitation gives the solution in which silver and chlorin are present in equivalent quantities. When silver is precipitated by a dilute bromid or iodid solution, the two points coalesce because the solubilities of silver bromid and iodid are so small that the amount precipitated by the first drop in excess is less than can be detected by the eye. Special calculations show that one part of solid silver chlorid in 3–5 millions parts of water gives a a perceptible turbidity. *W. D. B.*

On the Optical Rotation of Stereo-Isomeric Compounds. *Paul Walden. Zeit. phys. Chem.* **20,** 377 *(1896)*. Guye's theory of the «point of asymmetry» seeks to refer the amount of optical rotation to the *weights* only of the four groups attached to the asymmetrical carbon atom. The present paper, on the contrary, which contains measurements of the rotation of twelve ethers of *l*-amyl alcohol, shows that this property in question is largely influenced even by the subtle differences in constitution represented in stereochemical formulae. The molecular rotation of the diamyl ether of fumaric acid, for instance, differs from that of the corresponding maleic ether by more than 40 per cent of the value of the latter: the substances measured being liquids, all question as to the influence of the solvent is avoided. Incidentally the author has made the interesting observation, that the rotary power of the fluid itaconic ether is the same as is that of its polymer, the glassy brittle mass into which it is converted on standing. *W. L. M.*

Contribution to the Question as to the Cooperation of Chemical Affinity in the Process of Solution. *St. Tolloczko. Zeit. phys. Chem.* **20,** *412 (1896)*. Experiments have shown that in general the *d* and *l* modifications of optically active acids have the same solubility in water; but, if the process of solution involve the formation of additive products with the solvents (analagous to Pickering's hydrates) then «as the bodies produced by the solution of *d* and *l* forms in an optically active solvent may be seen, by the inspection of a stereochemical model, to be neither identical nor enantiomorphic in configuration» their solubilities in active solvents should be different.

Conversely, if experiment show the solubilities to be different, a strong argument will be furnished the supporters of the «hydrate theory» and at the same time a new method made available for the *dédoublement* of the racemic acids.

To put the matter to the test, the author dissolved racemic acid in water—in which it exists as a mixture of *d* and *l* tartaric acids—shook the solution with *l* amyl alcohol, extracted the acid from each phase separately and examined it in the polariscope. The same with mandelic acid. In both cases the results were negative: the *d* and *l* forms of both acids examined have the same solubilities, alike in the optically inactive water and in the active amyl alcohol.

W. L. M.

On Depression of Solubility. *St. Tolloczko. Zeit. phys. Chem.* **20**, *389* (*1896*). From measurements of the solubility of ether in water, and of the alteration produced by dissolving a third substance in the ether, the molecular weight of the substance in question may be calculated by well known formulae.

In a previous paper, *Ber. chem. Ges. Berlin*, **28**, *804* (*1895*) the author has shown how these quantities may be conveniently determined by the use of a suitably graduated flask, in which the ether and water may be shaken together, and the volume of the ether phase measured before and after the addition of the third substance.

The present article contains (*1*) a discussion of the precautions necessary to avoid errors from fluctuations in the temperature—a variation of 1/10° C may in unfavorable cases cause a difference of 10 per cent. in the molecular weight—see also *Jahrbuch der Chemie*, **5**, *19* (1896); (*2*) a table of the solubility of ether in water at intervals of 2° from 13°–21° C; and (*3*) a series of molecular weight determinations which show that, by this method, approximately «normal» results may be obtained with concentrations as high, in some cases, as 20 grams per 100 grams ether.

The author finds that the «depressions» in solubility observed by him are, with one exception, uniformly less—on the average about 10 per cent less—than those calculated from the molecular weight of the substance dissolved: he is unwilling to ascribe this discrepancy to an incipient polymerization, but leaves the question as to its origin unsettled. A plausible explanation may however be found in the consideration that water is probably less soluble in a mixture of ether with benzene, for instance, than in the same quantity of ether alone; if the addition of one gram mol. (78 grams) of benzene cause a diminution of 1/10 gram mol. (1.8 gram) in the

quantity of water in the ether phase, the discrepancy observed would be accounted for (*Cf.* Küster, *Ber. chem. Ges. Berlin* **27**, 327, 1894).
W. L. M.

Absorption and Dispersion of Light. *A. Cotton. Ann. chim. phys.* (7) **8**, *347* (*1896*). The rotation of the plane of polarized light by colored salt solutions varies with the wave length of the monochromatic light used. Measurements were made chiefly on solutions containing copper and chromium salts. With the double tartrate of potassium and chromium the effect is so abnormal that the same solutions are dextro-rotary for red and yellow rays and lævo-rotary for green and blue rays. *W. D. B.*

Different Modifications of Carbon. *H. Moissan. Ann. chim. phys.* (7) **8**, *289, 306, 466* (*1896*). These three memoirs give a connected account of the results which have appeared in the *Comptes rendus* during the last few years. Pure amorphous carbon seems never to have been obtained by anyone. Incomplete combustion of acetylene gave the best results and, next to that, the reduction of carbonic acid by boron. The two iodids of carbon, CI_4 and C_2I_4, did not yield carbon on decomposition, but a substance containing iodin. Amorphous carbon changes on heating, becoming denser and being less readily attacked by oxidizing agents. Whether this is due to a partial formation of graphite is not clear from the experiments; but this is probable since a sufficient rise of temperature converts amorphous carbon completely into graphite. The density of the amorphous carbon which has not been heated is 1.76.

Graphites are divided into two classes, those which froth with nitric acid and those which do not. Graphites formed from amorphous carbon or from diamond by elevation of temperature belong to the second class while all graphites obtained by crystallization from melted metals froth to a certain extent, that from melted platinum being the most striking in this respect. The frothing is possibly due to the formation of a small quantity of amorphous carbon but this point is not well established. No experiments were made to determine the effect of very slow cooling, though the presumption is that this would decrease the amount of the frothing graphite. Carbon vapor condenses to graphite in all cases. At atmospheric pressure carbon sublimes and does not melt. Boron and silicon precipitate carbon almost completely from melted iron. The precipitate is graphite if the temperature be not high enough to cause the formation of carbids. The densities of artificial graphites lie between 2.0 and 2.25. The author describes in detail the behavior of natural graphites from various sources. Most of these froth with nitric acid and have therefore not been formed directly from amorphous carbon or diamond.

To identify a substance as diamond it must scratch the ruby, have a density of about 3.5 and burn in oxygen with formation of the calculated amount of carbonic acid. No one of these tests by itself is sufficient nor are the first two taken together. The author discusses the finding of microscopic, black and transparent diamonds at the Cape of Good Hope, in the diamond-bearing sands of Brazil and in the meteorites from Cañon Diablo. After a brief critical *résumé* of the efforts of others to prepare artificial diamonds the author describes his own experiments. Working at ordinary pressures no diamonds were formed although many different metals were tried as solvents. Microscopic, black and transparent diamonds were obtained from iron and lead by cooling the surface of the metal suddenly so that crystallization took place under great pressure. From melted silver only black diamonds were obtained. If the pressure is sufficient, carbon crystallizes as transparent diamond; under a slightly lower pressure tarnished diamonds are formed and at yet lower pressures there appear black diamonds and a series of substances having properties varying continuously between diamond and graphite. There seems to be good evidence that at the highest temperatures the carbon separates from the solvent in the liquid form.

The memoirs furnish some very interesting though incomplete data for the physical chemist. At high temperatures graphite is the stable modification. Since diamond is denser than graphite it could have been predicted that crystallization experiments must be carried on under pressure. (In order to obtain large diamonds it will be necessary to devise some means of exerting enormous pressures and yet have the molten mass cool slowly.) The vapor pressure of carbon equals the external pressure at a lower temperature than that of the melting point. It seems certain that liquid carbon has a density exceeding 2.3 and it is probable that the density exceeds 3.5. The weak points in the paper are the change of amorphous carbon under the influence of heat and the distinction between graphites which froth with nitric acid and those which do not. The author is not familiar with the Phase Rule, and the coexistence of any number of modifications of the same substance presents no difficulties to his mind. A further investigation of the forms of carbon having densities of 2.5 to 3.5 is very much to be desired. Either these bodies are mixtures of graphite and diamond or they are solid solutions. Since no case is known of one modification dissolving in another without change, the former alternative is the more probable.

W. D. B.

Preparation of pure Chromium. *H. Moissan. Ann. chim. phys.* (7) **8**, *559* (*1896*). Melted quicklime will take most of the carbon out of chromium, and the nearly pure chromium can be freed entirely from carbon by converting it into the double oxid of chromium and calcium and reducing this compound in the electric furnace. The density of the pure metal is 6.92 at 20°C. Two compounds of chromium with carbon were obtained, CCr_4 and C_2Cr_3. These have not been studied from the point of view of the Phase Rule. Addition of carbon lowers the melting point of chromium.

W. D. B.

The Activity of the Kidneys in the Light of the Osmotic Pressure Theory. *G. Tammann. Zeit. phys. Chem.* **20**, *180* (*1896*). To force any of the solvent through a semipermeable wall, the external pressure upon the solution must be greater than the osmotic pressure of the solutes in respect to which the wall is permeable. Since filtration occurs through the glomerulus under a pressure of about 20 mm. of mercury and the partial pressures of everything except the albuminoids are greater than this value, it follows that this part of the kidneys can only be impermeable to albuminoids. Since these substances do not pass through the kidneys they are probably stopped here. The author shows that the increase in concentration of the filtrate from the glomerulus is not due to loss of water but to addition of urea and salts at some other point which can not yet be determined. *W. D. B.*

Quantitative Equilibrium.

Apparatus for Rapid Determination of the Surface Tensions of Liquids. *C. E. Linebarger. Am. Jour. Sci.* (*4*) **2**, *108* (*1896*). The author «measures the vertical distance betwen the lower ends of two capillary tubes when air under the same pressure issues in synchronous bubbles from their orifices.» An empirical equation gives the relation between this value, the density and the surface tension. The drawbacks to the method are a probable error of 0.1 *mm* (page 112) and the possibility of the «apparatus constant», changing from liquid to liquid. For the ten liquids studied the maximum variations in the «apparatus constant» are less than three per cent.

W. D. B.

Surface Tension of Mixtures of Normal Liquids. *C. E. Linebarger. Am. Jour. Sci.* (*4*) **2**, *226* (*1896*). The surface tensions of mixtures of toluene with benzene, turpentin, carbon bisulfid and ethyl benzoate can be calculated fairly accurately from the surface tensions of the pure liquids. This is not the case in any mixture containining ethyl oxid.

W. D. B.

On the Specific Heat of Sulfur in the Viscous State. *J. Dussy. Comptes rendus,* **123**, *305* (*1896*). The specific heat of viscous sulfur is higher than that of liquid sulfur and seems to have a point of discontinuity at about 230°. If sulfur be heated to 157°–175° and cooled suddenly a glassy modification is formed.

W. D. B.

Researches on the Volatility of Levulinic Acid. *M. Berthelot and G. André. Comptes rendus,* **123**, *341* (*1896*). Levulinic acid loses weight over sulfuric acid or lime ; but it is not clear what the dissociation products are. *W. D. B.*

Combination of Argon with Water. *P. Villard. Comptes rendus,* **123**, *377* (*1896*). A crystallized hydrate of argon has been formed with a dissociation pressure of about 105 atm. at 0°.

W. D. B.

Velocities.

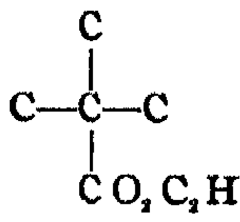
Additional concerning the Saponification of Alkyl-substituted Malonic Acid Esters. *Edv. Hjelt. Ber. chem. Ges. Berlin*, **29**, *1864* (*1896*). Measurements of the rate of saponification. The reaction was carried out at 16° C. in alcoholic (96%) solution containing per liter 1/20 mol. wt. in grams of the ether and an equivalent quantity of sodium hydrate, the residual alkali being titrated with fiftieth normal hydrochloric acid. The results cannot be expressed by the formula for bimolecular reactions, but the empirical formula

$$Ac = \frac{x}{a-x} \cdot \frac{1}{\sqrt{t}}$$

gives fairly contant values for *Ac*. Malonic ether and thirteen substituted malonic ethers were studied. The numerical results show that neither the affinity constant of the acid corresponding to the ether, nor the weight nor the volume—sum of the atomic volumes—of the substituting radical, is the sole factor determining the rate of saponification. The author suggests the influence of the stereochemical configuration in Bischoff s sense.

W. L. M.

On the Saponification of Certain Esters of Dibasic Acids. *Edv. Hjelt. Ber. chem. Ges. Berlin*, **29**, *1867* (*1896*). Measurements of the rate of saponification : composition of solutions and temperature as in the last notice. The percentage amount saponified at the expiration of 160 minutes was determined for seven ethers. As a result of all the measurements on ethers of di- and tri- basic acids it appears that ethers whose formulae contain the group : are especially difficult to saponify. *W. L. M.*



$$\begin{array}{c} \mathrm{C} \\ | \\ \mathrm{C}-\mathrm{C}-\mathrm{C} \\ | \\ \mathrm{CO_2C_2H_5} \end{array}$$

Measurements of the Velocity of Transformation of Diazoamido Bodies into Amido-azo Compounds. *H. Goldschmidt and R. U. Reinders. Ber. chem. Ges. Berlin*, **29**, *1369*, and *1899* (*1896*). Weighed quantities of diazoamidobenzene and of aniline hydrochloride were dissolved in aniline, at intervals a small portion removed, the reaction stopped by the addition of soda and the amount of diazo body remaining ascertained by boiling with water and measuring the nitrogen liberated. The authors found that the reaction is monomolecular, proceeding according to the formula

$$k=\frac{1}{t}\ log\ \frac{a}{a-x}$$

that the constant k is proportional to the concentration of the aniline salt, but almost independent of that of the diazo body, and that its variation with the temperature may be represented by van 't Hoff's formula, $log k= -A/T+B$. Further, that if the hydrochloride of aniline be replaced by the trichloracetate or dichloracetate the values of k are as 100:73:34 while the rates of inversion of sugar in aqueous solution by hydrochloric, tri- and dichloracetic acids respectively, are as 100:75:27 : this latter observation together with some others «makes it very probable that in aniline solution salts of aniline are decomposed into aniline and the acid». Experiments with homologous and substituted anilines and diazoamido compounds showed great variation in the value of k with the chemical nature of the reacting substances. *W. L. M.*

On the Influence of Pressure upon the Velocities of Reactions. *V. Rothmund. Zeit. phys. Chem.* **20**, *168* (*1896*). The rate at which cane sugar in aqueous solution is inverted by hydrochloric and nitric acids is less at high than at low pressures: the value of k (in the formula $dv=k.(a-x)dt$) decreasing about one per cent for each hundred atmospheres pressure, independently of the concentrations of the acid and of the sugar. [14°—16° C ; pressures up to 500 atm.]. The contrary is the case with the saponification of methyl and ethyl acetates by the same acids—the value of k *increasing* in this case about 4 per cent per 100 atm ;—it is consequently impossible to ascribe the effect altogether to alterations in the electrolytic dissociation of the acids ; the author, following a hypothesis of Arrhenius, considers it due to a change in the number of the «active» molecules of sugar and of the ethers respectively, and is confirmed in his view by finding that the results of his experiments may be expressed by a logarithmic formula (log $k=bp$, where p is the pressure and k the quotient of k for p atm. by k for one atm). Too much stress cannot be laid on this agreement however, as considerations analogous to those adduced by van 't Hoff (*Études p. 113*) with respect to the influence of temperature on the velocity of reactions, make it probable that in general the relation between rate and pressure may be represented by the equation $\partial \log k/\partial p = A/T$ of which the formula just quoted is a special case. The influence of neutral salts (KCl) seems independent of the pressure.

W. L. M.

On the Inversion of Sugar by Salts. *J. H. Long. Jour. Am. Chem. Soc.* **18**, *692*, *(1896)*. Salts formed from a weak base and a strong acid have the power of inverting sugar solutions. With most of the salts studied the reaction velocity constant increased during the course of the reaction. Whether this has anything to do with the formation of complex salts and setting free of acid was not shown. With ferrous salts the constant decreases rapidly but this seems to be due to the fact that these salts are unstable in the sugar solutions. Potassium alum gives a very good constant. It is a pity that no reference is made to the experiments of Kahlenberg, *Zeit. phys. Chem.* **17**, *577 (1895)*.

W. D. B.

On the Course of Chemical Reactions in Gases. *E. Cohen. Zeit. phys. Chem.* **20**, *303 (1896)*. The author points out that the reaction velocity for gases is a function of the walls of the vessel and illustrates this by experiments on arsine where the reaction velocity does not become constant until the walls are covered with arsenic. Since no term for the effect due the walls appears in the equation for reaction velocity the author thinks that Storch is not justified in concluding that the formation of water should be treated as a reaction of the ninth or twelfth order.

W. D. B.

On the Indirect Formation of Esters. *E. Petersen. Zeit. phys. Chem.* **20**, *331 (1896)*. The author admits that Tafel is right and that the increased velocity which he had observed is due to the action of the hydrochloric acid and not of methyl chlorid.

W. D. B.

On Compounds oxidizable under the Influence of the Oxidizing Ferment of Mushrooms. *E. Bourquelot. Comptes rendus*, **122**, *315 (1896)*. The action of this ferment on phenol ethers and aromatic amines is accelerated by the presence of acid.

W. D. B.

Electrochemistry.

Experimental Researches on the Electrolysis of Water. *A. P. Sokolow. Wied. Ann.* **58**, *209* (*1896*). Helmholtz has established an equation giving the electromotive force required to decompose water, in terms of the pressures of the gaseous hydrogen and oxygen in contact with the liquid water being decomposed. The gases may be kept separate or mixed and are not in contact directly with the electrodes. The equation is

$$V = V_o + 10^{-7}\eta T \left(R_H \frac{2H}{2H+O} \log_e \frac{p_H}{760} + R_o \frac{O}{2H+O} \log_e \frac{p_o}{760} \right)$$

where

V=potential difference at temperature T and pressures p_H, p_o ; V_o=potential difference at temperature and pressures 760 mm. mercury; T=absolute temperature ; η=electrochemical equivalent of hydrogen ; R_H=gas constant for hydrogen ; R_o=gas constant for oxygen ; H=atomic weight of hydrogen ; O=atomic weight of oxygen; p_H=pressure of hydrogen in mm of mercury p_o=pressure of oxygen in mm of mercury.

The present paper, to be followed by another, considers three things :—

1. A direct proof of the decomposition of water with indefinitely small potential differences.
2. The maximum pressure of hydrogen and oxygen at which electrolysis will take place with a potential difference of 1.070 volts.
3. A more accurate determination of the quantity V_o.

1. The first object was gained with the following apparatus : A voltameter is provided with horizontal platinum plates making the electrodes of the primary circuit. About 0.5 mm below the center of each electrode and normal to its surface is the free end of a platinum wire, the rest of the wire being insulated from the electrolyte by glass tubing, making the electrodes of the secondary circuit. The electrolyte is a ten per cent solution of sulfuric acid. The whole apparatus was repeatedly exhausted by an air pump.

On making a potential difference between the plate electrodes the author expected that if hydrogen and oxygen were set free, the two wire electrodes would be more or less charged by the hydrogen and oxygen which would diffuse to them through the 0.5 mm of electrolyte and show a potential difference. The expectation is justified by the results. With a potential difference between the plates of about 0.002 *D.*, a potential difference of about 0.0018 *D.* was produced between the wires. The wires did not, however, assume this difference at once but required about four hours and at the end of that time were still tending to a greater potential difference.

A similar behavior was observed with potential differences between the plate electrodes of from 0.002 *D* to 0.0048 *D.*

The author considers this a direct proof of the decomposition of water with a potential difference of 0.002 *D.*

2. The second object was not so easily gained, the results were very unsatisfactory.

An ordinary voltameter connected with an air pump and a MacLeod gauge was used and a potential difference of 1.070 volts was maintained between the platinum electrodes for 16 months. The electrolyte was a 25 per cent solution of sulfuric acid. The pressure of the mixed liberated gases continually rose and at the end of that time had reached 2.53 mm of mercury and was still rising. On this account no satisfactory conclusion regarding the maximum pressure corresponding to 1.070 volt could be drawn. However, the experiment showed that a potential difference of 1.070 volt would cause a very appreciable decomposition of water. In this same experiment 8.8 coulombs produced only 0.008 *mg* of free hydrogen and 0.064 *mg* of free oxygen, whereas 0.092 *mg* of free hydrogen and 0.732 *mg* of free oxygen should have been produced. The author concludes that electrolytic convection accounted for most of the 8.8 coulombs though probability of a secondary chemical change is considered.

3. The preceding experiments failing to give a relation between v and p, the potential difference necessary to produce a just visible evolution of gas was determined at varying pressures. The electrolyte was a 25 per cent solution of sulfuric acid. Substituting in the equation, V_0 could be determined. The results were not very con-

cordant, 7 per cent variation from the mean value of V_0; the author considers the values obtained at the lower pressures the more reliable; they give as a mean value

$$V_0 = 0.745 \text{ volts}$$

This corresponds to an osmotic pressure by the dissociated hydrogen and oxygen of

$$32.10^{-16} \textit{ mm} \text{ of mercury.}$$

The author considers this too small and consequently that the above value for V_0 is too large.

The experiments seem to have been very carefully conducted but the conclusions drawn by the author hardly appear justifiable. It appears extremely loose reasoning to claim that the behavior of a strong solution of sulfuric acid under those conditions is due to the water in it. The potential difference observed between the wire electrodes in the first series of experiments may very easily come from differences in concentration at the two electrodes as well as from chemical changes produced by the circuit. All one can really claim from this series of experiments is that there is evidence of a change at the given potential difference, but there is no direct evidence that water has been decomposed. A similar objection applies to the other experiments.

Clarence L. Speyers.

The Effect of Magnetism upon Electromotive Force. *Alfred H. Bucherer. Wied. Ann.* **58**, *564 (1896).* A critical review of the investigations on this subject, supplemented with a few new experiments. The author concludes :—

1. Magnetizing one of two iron electrodes in neutral solutions of ferrous salts does not produce a potential difference equal to 0.00001 V. Therefore the currents observed by Gross cannot be explained by a change in the chemical potential of the magnetized iron.

2. The currents observed on magnetizing an electrode are due to changes in concentration in the electrolyte when the magnetized electrode dissolves.

3. When ferric salts are in a mixed electrolyte, the direction of the current on magnetizing depends upon the concentration of the ferric salts at the two electrodes.

4. When the electrolyte contains ferrous salts but no ferric salts, the direction of the current, on magnetism, depends upon the concentration of all the iron salts at the two electrodes.

5. The primary currents of Rowland come from a shaking of the electrodes.

Clarence L. Speyers.

Electrolytic Reduction of Nitrobenzene in Solutions acidified with Hydrochloric Acid. *Walther Loeb. Ber. chem. Ges. Berlin,* **29,** *1894 (1896).* Nitrobenzene suspended in fuming hydrochloric acid and electrolyzed between platinum electrodes is converted (80 per cent) into *o*- and *p*- chloraniline: while if dissolved in a mixture of alcohol and hydrochloric acid the product is mainly benzidine hydrochloride. By a suitable arrangement of the apparatus the reaction may be made to furnish its own current: for example, by placing the nitrobenzene with about six times its weight of acid in a porous cell standing in a ten per cent solution of ferrous sulphate acidified with sulphuric acid, and establishing electric communication between a piece of gas carbon in the cell and a rod of amalgamated zinc in the outer solution, thirty grams of nitrobenzene were completely converted into *o*- and *p*- chloraniline in sixty-two hours. E.M.F. of the combination, one volt.

W. L. M.

On Convection Currents. *F. Richarz* and *C. Lonnes. Zeit. phys. Chem.* **20,** *145 (1896).* By means of the reaction with titanic acid, the presence of hydrogen peroxide may be recognized at the cathode when dilute sulphuric acid is electrolyzed by E.M.F.s too small to cause evolution of gas (less than 1.5 Daniell.) If the formation of this substance be due to the action of the hydrogen ions on dissolved oxygen, each gram molecule of the peroxide should correspond to a deposit of 2×107.9 grams of silver in a silver voltameter in the circuit: the maximum quantity actually measured was 83 per cent of this amount and was formed by conducting the electrolysis with an E.M.F. of 1 to 1.3 Dan. between electrodes of platinum saturated with hydrogen and oxygen respectively. When E.M.F.s less than one Daniell were employed no peroxide was formed. Similar experiments with solutions of sodium hydrate showed the formation of sodium peroxide (E.M.F. 2 Dan.); in baryta water no barium dioxide was formed.

W. L. M.

Influence of the Addition of Alcohol upon the Electrolytic Dissociation of Water. *R. Loewenherz. Zeit. phys. Chem.* **20**, *283* (*1896*). The author has made measurements of the E.M.F. at 25° C. of the combination Pt in H_2|0.01 HCl|0.01 LiCl|0.01 Na OH| Pt in O_2 in which the acid, salt and base are dissolved in mixtures of alcohol and water; and from these has calculated the electrolytic dissociation of the water in the mixtures, using the formula given in Ostwald's *Lehrbuch*, vol. **2**, page 901 and assuming that the E.M.F. at the boundaries of the lithium chloride solutions are unaffected by the presence of alcohol and amount to 0,0468 volt (calculated by Planck's formula for solutions in water.) The values thus obtained show a marked parallelism with the figures expressing the dielectric constants of the alcohol and water mixtures: the larger the percentage of alcohol, the less the dissociation of the water and the lower the dielectric constant.

An attempt is made to control these results by comparing them with values for the dissociation calculated on the assumption that the partial pressure of water vapor over mixtures of alcohol and water is proportional to the product of the concentrations of the H and OH ions in the mixture: these pressures however are not measured directly but are calculated from Abegg's determinations of the freezing point of aqueous alcohol; and in the cases worked out the difference between the two methods is «much greater than the probable experimental error» and is considered by the author to be due to «the influence of the nature of the solvent».

The discrepancy cannot however be accounted for in this manner, as the connection between the quantities involved may be shown without reference to any special theory of solutions, as follows:—if the hydrogen pole of one of L's cells (*e. g.* that with 24 per cent alcohol, E.M.F. 0,560 *V.*) be joined to the hydrogen pole of a similar cell whose solutions are made with pure water (E.M.F. 0,537 *V.*) and the circuit completed then—if no account be taken of differences between the two cells with respect to the phenomena at the boundaries of the lithium chloride solutions, *i. e.* if with Lowenherz the assumption be made that the E. M.F.s there are the same in both cells—the net result of the current (E.M.F. 0,023 *V.*) will be to transport water from the second cell to the first, and the electrical work gained ($2\varepsilon_0\pi$ for 18 grams of water) should be equal to $RT \log nat (p_2/p_1)$, that obtainable from a reversible gas engine working between p_1 and p_2, the partial pressures of the water vapor over the two solutions: or inserting the values of the constants (Ostwald l. c. page 827)

$$\log_{10}\frac{p_2}{p_1}=\frac{2\varepsilon_0\pi M}{RT}=\frac{2\times 96540\times 0.023\times 10^7\times 0.4343)}{8.36\times 10^7\times(273+25)}=0.7719$$

(L's method of calculation gives the same result without the factor *2*). Hence p_2/p_1 from E.M.F. is 5.92; calculated from freezing point determination (−14.6°C) it is 1.16;—conversely E.M.F. observed 0.023 *V.*; calculated from freezing point 0.002 *V.*

Assuming the accuracy of the experimental data in each case the difference may be due to variations in the E.M.F. at the lithium chloride solution or perhaps to alterations in the value of p_2/p_1 in the forty degrees between the freezing point and the temperature of the E.M.F. determination.

W. L. M.

Electromotive Force and Distribution-equilibrium: Priority-explanation. *A. H. Bucherer. Zeit. phys. Chem.* **22**, *328 (1896)*. On the strength of an article published in the *Elektrochemische Zeitschrift* **2**, 217 the author claims priority not only over Luther but apparently over everybody else: he says «I will only remark that the erection of a purely energetic theory of electrolysis has become possible only through my introduction of the vapor tension of the metals and the usual gas pressure of the gases as determining quantities in electrochemistry». In the present article the superiority of the Bucherer theory to the «Nernst-Ostwald views» is emphasized by an attack on R. Luther because the latter—after clearly showing how the direction of the current in a certain cell depends on the relative solubility of the zinc salt in the media employed—preferred to determine experimentally the direction and calculate the solubility instead of determining the relative solubility and deducing from that the direction of the current!

W. L. M.

The Transformation of the Energy of Carbon into other available forms. *C. J. Reed. Jour. Franklin Inst.* **July,** *1* *(1896).* The author first discusses the various methods for the transformation of the energy of carbon into more available forms, classifying them as follows: (1) Thermal, (2) Thermodynamic, (3) Thermoelectric, (4) Thermomagnetic, (5) Thermochemical. The last is discussed in detail and the conditions are presented under which, by this mode, a greater efficiency may be reached than by the others. The chief point claimed is that the most hopeful method for increasing the efficiency of transformation, relative to thermodynamic means, must involve the transfer of a part of the energy of the carbon into some other substance more easily oxidisable at low temperature, and hence better suited to the development of electrical energy in a galvanic cell. It is also pointed out that the ideal process should be cyclic except as regards the carbon consumed, and hence should involve the regeneration of all substances used as intermediate agents. These ideal conditions are represented by the following equations:

$$\begin{gathered} T+O=TO \\ C+T=CT \\ 2TO+CT=CO_2+3T \end{gathered}$$

Where T denotes the transforming substance and C and O combining equivalents of carbon and oxygen. The final result is CO_2, and the regeneration of the transforming substance. All of these reactions should be exothermal, and the first two as nearly athermal as possible.

It is found that substances realizing these conditions are nonmetallic. As an illustration the use of sulphur is discussed, the following operations being indirectly equivalent to those above stated.

Sulphur is first burned in air with reaction as follows:

$$S+O_2=SO_2+71000 \text{ heat units}$$

A part of the energy thus liberated is used to heat sulphur and carbon in a closed receptacle in the presence of steam and hot brick chips. The result is first the formation of CS_2 and then its decomposition into H_2S and CO_2. The SO_2 and H_2S then become the elements of a galvanic cell and may be used in either liquid solution, or in the gaseous form.

In the former, carbon electrodes are used, one set immersed in the H_2S solution and the other in the SO_2 solution. In the latter, a dilute H_2SO_4 electrolyte is used, into which hollow carbon electrodes containing the gas under pressure are placed.

The reaction within the cell is as follows:

$$\left.\begin{matrix}2H_2S\\272000\end{matrix}\right\}+\left.\begin{matrix}SO_2\\0\end{matrix}\right\}=\left.\begin{matrix}2H_2O\\0\end{matrix}\right\}+\left.\begin{matrix}3S\\213000\end{matrix}\right\}+\left.\begin{matrix}\text{Heat or Elec-}\\\text{trical Energy}\\59000\end{matrix}\right\}$$

The sulphur having been regenerated, its ultimate expenditure is one equivalent of C, or 97000, from which a return is obtained of 59000. This gives an efficiency of 0.61. Actually various losses occur, the nature of which is discussed, their effect being the reduction of the actual efficiency to about one-half of this amount. The ideal E.M.F. is shown to be 0.63 volts, whereas experimentally an E.M.F. of 0.32 to 0.36 volts has been attained, thus indicating an efficiency of about 35 per cent.

The paper is commendable for clear statement of the lines along which this author believes investigation must follow in order to increase the efficiency of transformation of energy from carbon, and for the presentation of a simple set of illustrative reactions by which a relatively high efficiency may be attained. At the same time as the author notes, this particular set of operations is not presumably the best obtainable, nor are the results of such a nature as to guarantee success upon a commercial basis. From the amount of attention which this problem is now attracting, we may perhaps expect in the near future a multiplicity of possible methods for its solution. The placing of these upon a commercial basis is, however, a different matter; and it is here probably that the greatest difficulty will be encountered, and in this direction that new effort must be most largely directed. *W. F. Durand.*

On the Temperature-coefficients of the E.M.F. of Certain Galvanic Combinations of Silver and Silver Salts. *J. M. Lovén. Zeit. phys. Chem.* **20,** *456 (1896).* In a paper on «The Thermochemistry of the Ions» (*Zeit. Phys. Chem.* **11,** *501, 1893*) Ostwald has developed the theory of galvanic combinations of the type Ag | $AgNO_3$ | KNO_3 | AgCl in KCl | Ag and has shown that such a combination may be treated either as a «concentration» cell, according to

Nernst's theory, or as a «chemical» cell according to that of Gibbs and Helmholtz; but that the expression arrived at for the temperature coefficient of its E.M.F. is the same in either case.

In the present paper the author communicates the results of experimental determinations at 15° C and 77° C of the E.M.F. of cells of the type under consideration, made up with *n/10* salt solutions and the chloride, bromide, and iodide of silver respectively. The temperature coefficients are in every case found to be ***negative***, in conformity with the theory; their numerical values differ from those calculated by from seven to sixteen per cent.

W. L. M.

On Contact Electricity. *A Résumé, W. Nernst. Wied. Ann.* **58**, *Beilage No. 8* (*1896*). The author first passes in review the various methods that have been from time to time suggested for *measuring* the E.M.F. of the contact of two homogeneous bodies: (*a*) Volta's method, by means of condenser experiments, has long been abandoned as neglecting the influence of the air; (*b*) Edlund's method, from measurements of the Peltier effect, is characterized by the author as «based on a purely arbitrary assumption, and in flat contradiction with the results of experiment as represented in W. Thomson's equation». Of the two remaining methods, both of which are derived from Helmholtz's theory of the electrocapillary phenomena, one, viz:—(*c*) that depending on measurement of the maxium capillarity of polarized mercury, has at all events the merit of necessitating only such measurements as can be carried out accurately in the laboratory, while the other, (*d*), that involving electrodes of dropping mercury, «yields in practice results so contradictory as to be of hardly any value».

Then come the methods of *calculating* the E.M.F., developed as yet only in the case in which one, at least, of the bodies in contact, is an electrolytic solution. All of these are referred to the fundamental ideas expressed in the equations of the author and of M. Planck; they involve a knowledge of the relative velocities of the ions and of their concentrations in the solutions under consideration. «In the uniform coincidence between the values experimentally obtained, and those calculated, for the E.M.F. of the most varied galvanic combinations, the figures obtained from the osmotic theory have found a thoroughgoing conformation ; the values obtained from the use of Helmholtz's theory, on the other hand, have as yet proved inaccessible to independent control».

The electrocapillary phenomena are next subjected to an analysis from the standpoint of the osmotic theory, an explanation is found for the erratic results of measurements with the dropping electrodes, and a modification in the mode of using them is suggested : the result of the discussion is that «although from the qualitative point of view Helmholtz's theory of the electrocapillary phenomena appears to be in full accord with the osmotic theory, yet a quantitative comparison reveals noteworthy contradictions between them».

As an example of the contradictions in question may be quoted the combination Hg | KCl | KI | Hg, where the algebraic sum of the three E.M.F.s calculated—the first and third from Helmholtz's theory, the second from that of Planck—differs from the E.M.F. of the cell as experimentally determined, by more than four-tenths of a volt ! The author discusses briefly the possible nature of the modification in the theories necessitated by cases such as this.

A note on pyro- and piezo-electricity closes the article, which though short (thirteen pages in all) is well worth careful attention. The discrepancy between the theoretical and experimental results quoted in the preceding paragraph certainly goes to show that the «problem of the century» is not so near solution as has generally been supposed. *W. L. M.*

Oxidation of Sodium Sulfid and Hydrosulfid. *F. W. Durkee. Am. Chem. Jour.* **18**, *525 (1896)*. When sodium sulfid is electrolyzed there are formed polysulfids and sodium hydroxid, then sodium thiosulfate and sulfur, and finally sodium sulfate. When the reaction is followed quantitatively it is found that the sulfids disappear first, then the thiosulfate and lastly the hydroxid. The statement of the author that the thiosulfate is the last to disappear is not in accordance with the published data. *W. D. B.*

The Electrolysis of Hydrochloric Acid. *G. O. Higley and B. J. Howard. Am. Chem. Jour.* **18**, *584 (1896)*. The hydrogen and chlorin are caught in inverted U-tubes instead of in straight burettes. In this way the gases pass through a smaller layer of liquid than usual and there is less absorption. When working under diminished pressure the results are said to be satisfactory enough for a lecture experiment. The description of the apparatus is not clear and the accompanying diagram is not very satisfactory. *W. D. B.*

The Action of Metals on Nitric Acid. *G. O. Higley and W. E. Davis. Am. Chem. Jour.* **18**, *587* (*1896*). There is no nitrous oxid formed by the action of silver on nitric acid, while this substance is formed when lead or copper is used. The authors are inclined to believe that the metal acts directly on the nitrate part of the acid. The experiments of Gladstone and Tribe established this point many years ago. It is not probable that much progress will be made until the effects due to the metal and to nascent hydrogen are carefully distinguished.
W. D. B.

Action of Mercury Salts on Aluminum. *P. A. E. Richards. Chem. News,* **74**, *30* (*1896*). Reference is made to the formation of aluminum oxid from aluminum amalgam. The author is ignorant of the fact that the phenomenon was described nearly twenty years ago by Jehn. *Ber. chem Ges. Berlin,* **11**, *361* (*1878*).
W. D. B.

Calculation of the Conductivity of Mixtures of Electrolytes having a Common Ion. *D. McIntosh. Chem. News,* **74**, *23, 35, 44* (*1896*). The author finds that the conductivity of mixtures of sodium chlorid and hydrochloric acid and of sodium chlorid and potassium chlorid can be calculated with a fair approach to accuracy when the solutions are not too concentrated. The calculated values do not agree so well with those found directly when the concentration of the two substances is more than one gram-molecule per liter.
W. D. B.

Note on the Degree of Dissociation of Electrolytes at Zero Degrees. *M. Wildermann. Phil. Mag.* [*5*] **42**, *102* (*1896*). It is pointed out that the conductivity at infinite dilution has not been determined directly by Wood at 0°C. and that it is very desirable this should be done. *W. D. B.*

Electrolytic Process for the Extraction and Separation of Metals. *D. Tommasi. Bull. Soc. Chim.* (*3*) **15**, *838* (*1896*). By means of a revolving cathode and scraper it is possible to remove the metal as fast as formed or after it has reached any desired degree of thickness. In this way the metal is removed from the action of the bath and polarization is largely avoided. *W. D. B.*

On Potential Differences at the Surfaces of Dilute Solutions. *O F. Tower. Zeit. phys. Chem* **20**, *198* (*1896*). This paper is intended to show that Planck's formula is applicable to a cell of the type MnO_2|Acid|KCl|Acid|MnO_2 and that the electromotive force of these cells differs from that of the combination MnO_2|Acid|Acid|MnO_2 chiefly by the potential difference between the acid solutions in the latter case. His experiments confirm both conclusions fairly well, the error being about one millivolt in a total of thirty. Sodium chlorid satisfies the second conclusion better than potassium chlorid, rather to the author's surprise. The author has not shown that Planck's formula requires the second conclusion to be fulfilled when the migration velocities of the cation and anion are equal in the salt solution; but assumes it as self-evident. One interesting fact appears in the paper, that Zn|$Zn(NO_3)_2$ does not give a constant potential difference. The author does not refer this to the action of metallic zinc on zinc nitrate as he should. It would be interesting to know what hypothesis could be devised in respect to which the experiment recorded in table 10, page 206, could prove anything either way. *W. D. B.*

The Electrolytic Decomposition Tension of Melted Zinc Chlorid. *R. Lorenz. Zeit. anorg. Chem.* **12**, *272* (*1896*). Melted zinc chlorid was decomposed between carbon electrodes at a potential difference of 1.5 volts. Since the temperature was higher than that at which zinc melts the zinc dropped down from the electrode. It would have been very interesting to have had some determinations of the cathodic polarization under these circumstances.

W. D. B.

Correction—Page 31, line 8: for $n=h$, read $n-h$

SOLUTION AND FUSION

BY WILDER D. BANCROFT

If phenanthrene be added to naphthalene[1] the freezing point of the latter is lowered and the depression increases with further addition of phenanthrene until the solution has the composition of the eutectic alloy[2] when naphthalene and phenanthrene crystallize side by side and the solution solidifies without change of temperature. If naphthalene be added in ever increasing quantities to phenanthrene the freezing point of the phenanthrene is lowered until the temperature is again reached at which the eutectic alloy freezes. This is shown qualitatively in Fig. 1. The ordinates represent temperature and the abscissae the percentage composition of the solutions; at the left being naphthalene, at the right phenanthrene.[3] Along the curve AB the solutions are in equilibrium with solid naphthalene, along BC with solid phenanthrene while the point C, at the intersection of the two curves, shows the temperature and the composition of the solution at the quadruple point where the four phases co-exist, naphthalene, phenanthrene, solution and vapor. These two curves are fusion curves and naphthalene is the solvent, phenanthrene the solute in the solutions which are in equilibrium with solid naphthalene, while these terms are reversed for the solutions in equilibrium with solid phenanthrene.[4]

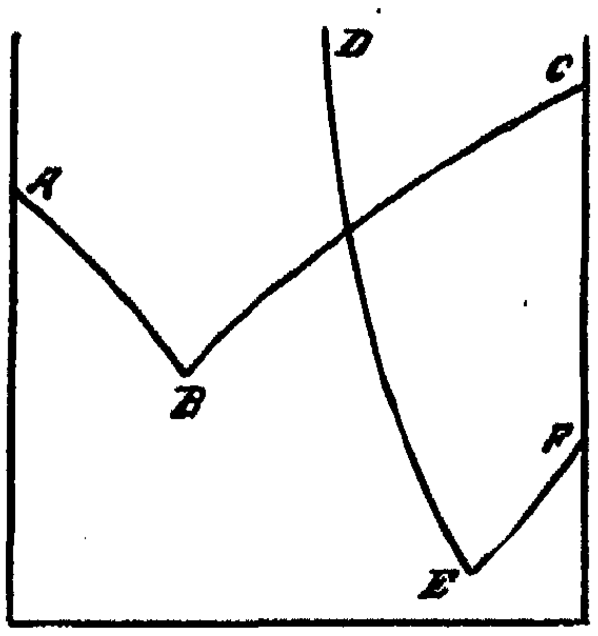


Fig. 1.

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[1] Miolati. Zeit. phys. Chem. 9, 649 (1892).

[2] Guthrie. Phil. Mag. (5) 17, 462 (1884).

[3] Cf. Konowalow. Wied. Ann. 14, 40 (1881).

[4] Bancroft. Phys. Rev. 3, 20 (1895).

Suppose that instead of these two substances we take potassium chlorid and water as the two components. We find a series of solutions in equilibrium with solid potassium chlorid and a series of solutions in equilibrium with ice; these, if plotted as before, will give two curves intersecting at the temperature of the cryohydrate in the quadruple point. This is represented in Fig. I by the lines DE and DF, potassium chlorid being at the left and water at the right. At first sight it seems as if these were both fusion curves and that in one set of solutions water is dissolved in potassium chlorid, in the other potassium chlorid in water. This view is adopted by most people[1]; but a very slight consideration will show that it is incorrect. In the case first considered the two components are miscible in all proportions at any temperature at which both are liquid, a condition the importance and significance of which is often overlooked.[2] We cannot tell whether this is so in the case of potassium chlorid and water because the salt melts at too high a temperature. It will therefore be better to take two substances with melting-points lying within the range of experiment, such as naphthalene or phenol and water. It is possible to make a series of solutions in equilibrium with solid naphthalene and another set in equilibrium with ice. There is no dispute about the second set of solutions. The curve representing them is a fusion curve and water is the solvent. The accepted doctrine in regard to the other set is that, in so far as one makes a distinction between solvent and solute at all, the naphthalene is the solvent and the curve representing the solutions is a fusion curve.[3] My own view is that the curve is a solubility curve and that naphthalene is the solute. The point at issue is whether solubility and fusion curves are always or even ever identical. The first part of the question can be answered off-hand in the negative. With partially miscible liquids, such as ether and water, one of the liquid phases is a solution of ether in water, the other of water in ether and the compositions of the phases at different temperatures give two solubility curves when represented graphically.

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[1] Le Chatelier. Equilibres chimiques, 130; Nernst. Theor. Chem. 394.

[2] Ostwald. Lehrbuch **I**, 1037; Riecke. Zeit. phys. Chem. **7**, 422 (1891); Schröder. Ibid. **11**, 452 (1893).

[3] Ostwald. Lehrbuch **I**, 1024; also Zeit. phys. Chem. **12**, 394 (1893).

These cannot be called fusion curves because the temperature of the experiment is above the fusion temperature of either of the components. The other part of the question is best answered by a study of the diagram for naphthalene and water (Fig. 2). At the left is one hundred per cent naphthalene, at the right one hundred per cent water, while the ordinates represent temperature. The diagram is not to scale because all the the solubilities are unknown. In the figure, A represents the fusion temperature of pure naphthalene and AB the depression of the freezing-point by continued addition of water. AB is therefore the fusion curve for naphthalene in presence of water, naphthalene being solvent. Between 74° and 80°, there can exist also the system composed of two liquid phases and vapor. The hypothetical compositions of the two solutions are shown by the curves BC and DE. These two are entirely analogous to the curves representing the two liquid layers formed by mixing ether and water; they are therefore solubility curves, DE being the curve for the saturated solution of naphthalene in water, BC for the saturated solution of water in naphthalene. The curves AB and CB cannot be identical because in that case we should have solid naphthalene in equilibrium with two liquid phases and vapor over a range of temperatures, which is impossible. At B the fusion and the solubility curves become identical and at the temperature of about 74° there is equilibrium between the four phases, solid naphthalene, water in naphthalene, naphthalene in water and vapor. The curves BC and DE meet at some unknown temperature without much doubt.[1] At any temperature below that of the quadruple point, we have only solid naphthalene, naphthalene in water and vapor until the cryohydric temperature is reached at F. This equilibrium is shown by

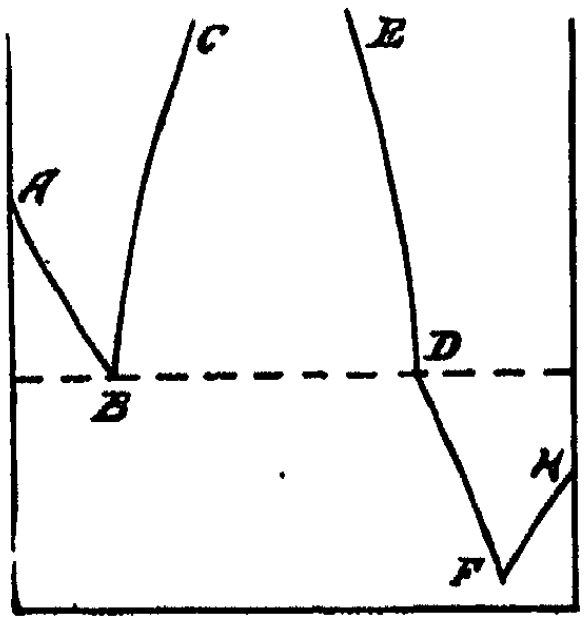

Fig. 2.

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[1] Alexejew. Wied. Ann. **28**, 305 (1886); Masson. Zeit. phys. Chem. **7**, 500 (1891).

the curve DF which is neither a continuation of AB nor of CB, but of ED. It has a slightly different inclination from ED because the naphthalene now separates in the solid form and the heat of solution is much greater.[1] The last curve in the diagram, HF, is the fusion curve for ice in the presence of naphthalene. It can not be identical with DF for the same reason that AB can not be CB, that it would involve a breach of the Phase Rule. We see from this that a fusion curve is never a solubility curve and *vice-versa*. Also that the solubility and fusion curves cease to be stable after their intersection. Below the inversion temperature neither of the two curves can exist except as a labile modification.

I have illustrated this point by a reference to the equilibrium between naphthalene and water to show that the question can be settled by an application of the Phase Rule to the facts without any quantitative data being known. This does not imply that there are no quantitative data. Alexejew has made a study of benzoic acid and water which is quite sufficient for our purpose. The main features of his diagram are reproduced in Fig. 3, benzoic acid being at the left and water at the right. AB is the fusion curve when water is added to benzoic acid, LBM the solubility curve for water in benzoic acid, of which the labile part BM has actually been realized. LDN is the solubility curve for benzoic acid in water, the part DN being a supersaturated solution. From these solutions the benzoic acid precipitates in liquid form. The two curves MBL and NDL meet at L, the two substances being miscible in all proportions at higher temperatures. DF is the solubility curve for benzoic acid in water, the solute separating as crystals, while the curve FH is the fusion curve for ice in the presence of benzoic acid. Owing to the sparing solubility of the latter

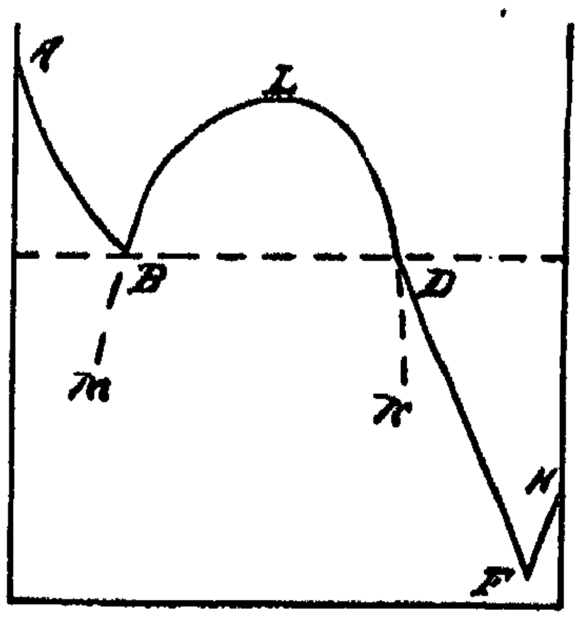

FIG. 3.

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[1] Walker. Zeit. phys. Chem. 5, 192 (1890).

in cold water this curve is very short and was not determined by Alexejew. It is thus clear that in all saturated solutions to the left of the point L the solvent is benzoic acid whereas to the right of this point water plays that part.

In the case of benzoic acid and water, only a short portion of the curves ML and NL corresponded to labile modifications; but with salicylic acid and water the two liquid layers can exist only as labile forms. This will be clear from the diagram (Fig. 4) illustrat- this case. Water is as before at the right. The curves MLN can only be obtained by working under pressure in sealed tubes. AB is certainly the fusion curve of salicylic acid in the presence of water and FD equally certainly the solubility curve of salicylic acid in water; but where the one changes into the other or what BD actually represents is very uncertain. It is much to be desired that someone should make a careful and exhaustive study of the vapor pressures of this system.

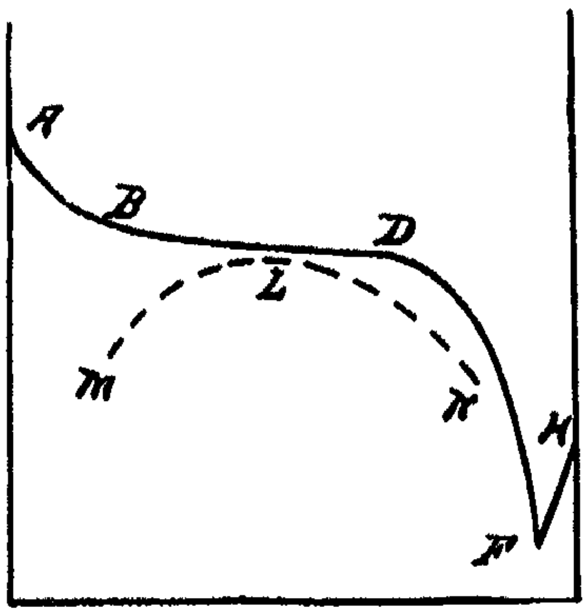

Fig. 4.

A curious point occurs in the behavior of sulfur dioxid and water, investigated by Bakhuis Roozeboom.[1] It is possible at the same temperature to have the solid hydrate $SO_2 7H_2O$ in equilibrium with vapor and a solution of sulfur dioxid in water or with vapor and a solution of water in sulfur dioxid. These cannot be fusion curves because Stortenbeker[2] has shown that it is not permissible to apply the Theorem of Raoult-van 't Hoff when the solute would be a component of the solvent. We must interpret the phenomena something as follows: The first solution is saturated in respect to sulfur dioxid and tends, if more be added, to form two liquid layers; the new phase is instable and changes into the solid hydrate. In the second instance the solution is saturated in respect to water and

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[1] Recueil Trav. Pays-Bas 3, 29 (1884); 4, 65 (1885); also Zeit. phys. Chem. 2, 450 (1888).

[2] Ibid. 10, 194 (1892).

an excess precipitates as a solution instable in presence of the other phases and therefore changing into the solid hydrate. In other words the hydrate results from the precipitation of sulfur dioxid in one case and of water in the other. This explanation is not so far-fetched as it may seem. Frankenheim[1] and others have shown that when salts are precipitated by alcohol there is formed first an instable liquid phase from which the salt then separates. This can be seen without the microscope if alcohol be added to a strong solution of sodium carbonate. The second liquid phase, although instable, does not disappear for quite a while. It is well known that when melted sulfur is poured into water it solidifies in a labile modification. I have noticed that the addition of water to a solution of mercuric iodid in methyl alcohol precipitates the yellow modification although it is instable at room temperatures. It will do this even when the red crystals are present. It seems as if one might make the generalization that the less stable form is the first to appear in the case of sudden precipitation.

While water is solvent in one of the solutions in equilibrium with the hydrate, $SO_2 7H_2O$, and solute in the other, it is solvent in both of the solutions in equilibrium with the hydrates of calcium or ferric chlorid.[2] The difference here is that there are never two liquid layers in equilibrium and there is no reason for assuming that in any of the cases is the water dissolved in the salt. I prefer to look upon the solutions containing more of the solid than the hydrate as stable, supersaturated solutions although this may seem a contradiction in terms. For a given temperature the vapor pressure of a hydrated salt can not fall below a certain value without the salt efflorescing. The saturated solution under discussion has that vapor pressure and as the solution would become more concentrated if the hydrate crystallized out, its vapor pressure would fall below the lowest value at which the hydrate could exist. Therefore the hydrated salt can not crystallize out although the solution is supersaturated in respect to it. It is thus possible, in certain well-defined cases, for a solution to be stable in the presence of the solid phase in respect to which it is supersaturated.

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[1] Ostwald. Lehrbuch I, 1040–1043; [2] Bakhuis Roozeboom. Zeit. phys. Chem 4, 31 (1889); 10, 477 (1892).

The distinction between a fusion and a solubility curve has been recognized for a long time although no one has called attention to it. The approximation formulas for the change of concentration with the temperature have the same form for both curves, except that the heat of fusion enters into one[1] and the heat of solution into the other[2]. Since these two quantities are not identical, it follows that there is a radical distinction between the two curves.[3]

There remains still a point to be considered. In the first case taken up in this paper, that of naphthalene and phenanthrene, it was found that, instead of four curves as with naphthalene and water, there were only the two fusion curves because the two melted components were consolute *i. e.* miscible in all proportions. It does not follow because two liquids are consolute that each has not a definite solubility in the other. This can be seen from Fig. 5. The ordinates represent temperature and the abscissae the percentage compositions of the solutions. There are two definite solubilities below the temperature T and there can co-exist two liquid phases if the substances be taken in proper proportions. At T each liquid has a definite solubility in the other; but the two saturated solutions are identical in composition. For this reason there cannot be two liquid phases co-existing and we have at this temperature two liquids miscible in all proportions, each having a definite and known solubility in the other. At higher temperature there are two possibilities. The solubilities may both become infinite as represented by the dotted line TA and TB

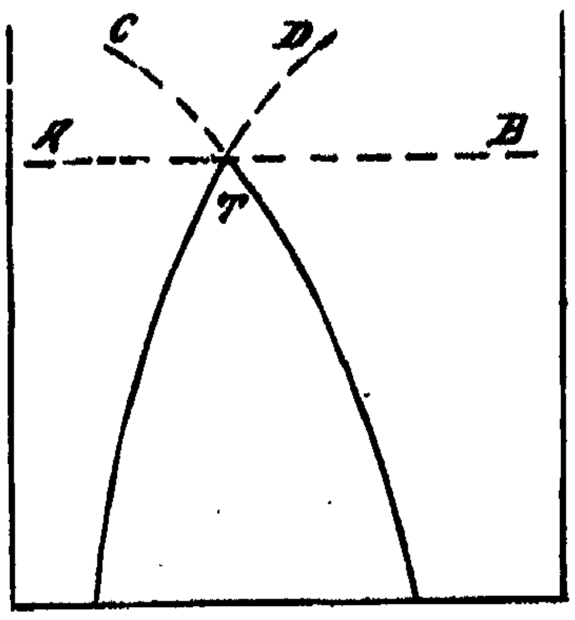

Fig. 5.

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[1] van 't Hoff. Lois de l'équilibres chimiques, 46; also Ostwald. Lehrbuch I, 760.

[2] van 't Hoff. l.c. 36; also Nernst. Theor. Chem. 515.

[3] Linebarger, Am. Jour. Sci. 49, 48, (1895), has attempted to apply the Schröder-Le Chatelier Theorem for fusion curves to solubility curves—naturally without success.

or they may not, as illustrated by the dotted lines TC and TD. There is a third possibility that one of the solubilities may become infinite and the other not; but that is rather a combination of the other two cases than a new one. The first case is tacitly assumed to be the type of all pairs of consolute liquids and needs no discussion. It will be profitable to consider the second case. Above what may be called the consolute temperature[1] the liquids have each a solubility in the other; but two liquid phases can not co-exist because the two solubilities overlap, so that a mixture which is supersaturated in respect to one component as solute is unsaturated in respect to the other. (Two liquid phases are formed only when the mixture is supersaturated in respect to both components). There is thus no theoretical reason to prevent the assumption of definite but overlapping solubilities[2] in the case of two consolute liquids and the only question is whether instances of this actually occur. If the two solubility curves cut each other at an angle at the consolute temperature, the solubilities can not become infinite immediately after passing that point. This is the case for the solubility curves in the diagram (Fig. 5) which represents the experimental data for sulfur and toluene,[3] sulfur being at the left. Of course this effect is influenced very largely by the scale used and it is open to anyone to change the abscissae and to say that there is no angle and that the curve is continuous through the consolute temperature. A more extended series of very careful measurements would help matters somewhat; but it is probable that the question can only be settled by a study of the behavior of the liquids above the consolute temperature. It now

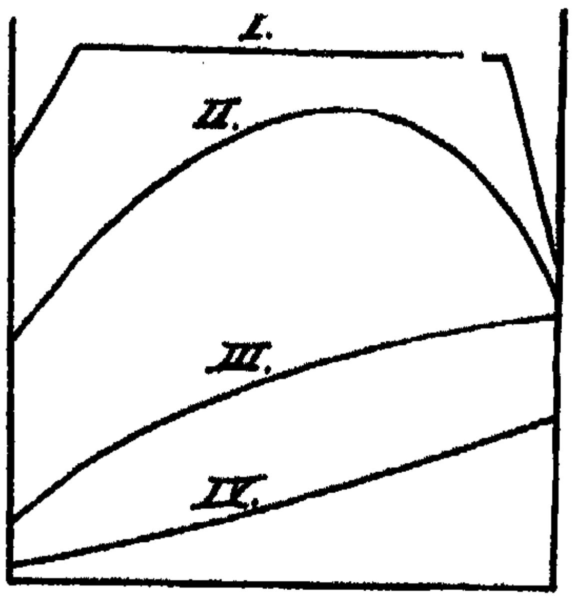

Fig. 5.

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[1] "*Mischungstemperatur*" of Alexejew.

[2] Since writing this I have been surprised and pleased to find the same idea stated clearly by Horstmann. Graham-Otto's Lehrbuch **I**, 32 (1885).

[3] Alexejew. Wied. Ann. **28**, 310 (1886).

becomes probable in view of this one instance that it is the exception rather than the rule that the solubilities become infinite at the consolute temperature. There is indirect experimental evidence in favor of this view. We know that in a homologous series of organic compounds the miscibility with water increases with decreasing amount of carbon[1] and there is no reason to assume that this ceases to be true after the liquids become consolute. In Fig. 6 are rough reproductions of the general form of pressure curves found by Konowalow[2] for isobutyl, propyl, ethyl and methyl alcohols with water, numbered I, II, III and IV respectively. The ordinates are pressures but are not measured from the same zero. The abscissae are percentage compositions, water being at the left. Isobutyl alcohol is only partially miscible with water, the others miscible in all proportions. Instead of having the same type of curve in the last three cases, it is evident that, as one passes from propyl to methyl alcohol, there is a regular change in the form of the vapor pressure curve as the mutual solubilities increase. We may therefore conclude that each of these three alcohols, propyl, ethyl and methyl, has a definite solubility in water and that the same is true for water in the three alcohols. A natural corollary would be that the first of any series of homologous compounds to be completely miscible with a given liquid might be expected to behave like propyl alcohol and water, giving a mixture with a constant boiling point lower than that of either pure component; but this needs to be made more definite.

If, just below the consolute temperature, the vapor pressure of the system, two liquid layers and vapor, is higher than that of either component at that temperature, the vapor pressure curve for these two substances will have a maximum at temperatures just above the consolute temperature. If, just below the consolute temperature, the system, two liquid layers and vapor, has a vapor pressure lying between those of the two components at that temperature the vapor pressure curves for these two substances will not have a maximum just above the consolute temperature. The first type will present a

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[1] Ostwald. Lehrbuch I, 1065.

[2] Wied. Ann. 14, 34 (1881) also Ostwald. Lehrbuch I, 647.

minimum boiling point if made to boil in the neighborhood of the consolute temperature ; the second type will not. At temperatures well above the consolute temperatures a maximum vapor pressure for some concentration is no longer necessary. Phenol becomes miscible with water in all proportions at about 70° ; but no mixture of these two substances boil below 100°. It is not known whether, under diminished pressure, a maximum would appear or whether the vapor pressure of phenol and water at 65° is lower than that of water at the same temperature. In connection with this I may say that a mixture of sulfur and toluene gives two liquid layers with a boiling point between those of the two pure components. So far as I know this is the first authentic instance of such a phenomenon occurring in an open vessel at atmospheric pressure, since sulfur dioxid and water show this only at a pressure of over two atmospheres[1] while the case of amylvalerate and water cited by Ostwald[2] seems a very doubtful one. Sulfur and xylene show the same thing in a more marked fashion and it would not be difficult now to multiply instances indefinitely.

That in a solution one substance is solvent and the other solute has been recognized by Nernst in his treatment of the case when both components have an appreciable vapor pressure[3]. While he allows the vapor pressure of the solvent to vary according to the Theorem of van 't Hoff, he assumes that the partial pressure of the solute follows the Theorem of Henry. This is, by the way, an assumption which he does not prove ; but the point of interest here is that he is forced to treat the two components differently. This does not seem to have been clearly understood by Beckmann[4] if I have read his very obscure sentence correctly. While accepting without reserve Nernst's dictum that the Theorem of Henry holds for all solutes, he is surprised that the partial pressures of iodin vapor are not the same in solutions of the same strength with different solvents.[5] There is nothing in Henry's Theorem to the effect that

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[1] Roozeboom. Recueil Trav. Pays-Bas. **3**, 38 (1884) ; Zeit. phys. Chem. **8**, 526 (1891).

[2] Lehrbuch **I**, 643.

[3] Theor. Chem. 388.

[4] Zeit. phys. Chem. **1**, 131 (1895).

[5] Ibid. 132.

the absorption coefficient of a gas is the same for all solvents[1]. Nernst has not carried this differentiation further; but he has made another statement on the subject of partial pressures which is worthy of our attention. He says:[2] «The partial pressure of each component of a mixture is always less than its vapor pressure in the pure state (solid or liquid) at that temperature.» This is not accurate. Nernst himself has stated[3] that, at the freezing point of a solution, the vapor pressure of the solvent is the same for solution and for pure solid solvent. He would admit this for the solute in the case of a saturated solution. His principle is thus seen to be wrong in the form in which he has stated it. It is open also to a theoretical objection which has been entirely overlooked. From the Theorem of LeChatelier[4] it follows that when one substance is dissolved in another, some of the vapor of the solvent will condense in order to reduce the concentration of the solute. The partial pressure of the solvent is therefore always less than its vapor pressure as a pure liquid at the same temperature. This proof applies only to the solvent. The same result would be obtained if the solute became more volatile. It is therefore possible for the vapor pressure of the solute to be greater or less than its vapor pressure in the pure state, depending on conditions with which we are not yet familiar. It seems certain that the partial pressure of the solute can not be raised above the vapor pressure which it would have were it present as a liquid at that temperature and that the effect can occur only with solutes which are normally solid at the temperature of the experiment. That the presence of a second substance may increase the partial pressure of the first would seem to follow from Hannay's[5] experiments on the solubility of solids in gases and from those of Villard[6] on the solubility of iodin in carbonic acid. It seems very difficult to account for the results of Gooch[7] unless the vapor pressure of the boric acid is increased by the presence of the solvent. This possibility has not been taken into account by Ostwald[8] in his

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[1] Ostwald. Lehrbuch **I**, 617.
[2] Theor. Chem. 97.
[3] Ibid. 97, 128.
[4] Ibid. 526.
[5] Proc. Roy. Soc. **30**, 178 (1880).
[6] Comptes rendus, **120**, 183 (1895).
[7] Proc. Am. Acad. **22**, 167 (1886).
[8] Anal. Chemie, 33.

treatment of distillation with a vapor current although he has explicitly admitted the solubility of solids in vapors[1]. It may be urged that the effect would be infinitely small at ordinary temperatures and pressures; but this has nothing to do with the theoretical side of the question. If the effect takes place at any temperature and pressure we have no right at present to assume that it does not also occur at any other temperature and pressure. As for its being infinitely small at ordinary temperatures, no one has ever tried to see whether there might not be cases where the influence of the second component was really measurable. It is very unsafe to base a general statement on the fact that you have not found a thing you never looked for. Ostwald's view is that if one works with a saturated solution it is immaterial what vapor one uses as an aid in distilling solid substances having a low vapor pressure at the temperature of the experiment. Whether this is so cannot be answered definitely as there is no quantitative evidence either way; but there is good reason to suppose that this position is untenable.

The results of this paper may be summed up as follows:—

1. Solubility and fusion curves are never identical.
2. A solubility curve may seem to be a continuation of a fusion curve.
3. Two consolute liquids may have definite solubilities, one in the other.
4. The partial pressure of a solid solute may be greater than its vapor pressure in the pure state.

Cornell University; January, 1896

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[1] Lehrbuch I, 612.

SPEED OF ESTERIFICATION, AS COMPARED WITH THEORY

BY ROBT. B. WARDER

I. Introduction

The following paper is based upon the theory of mass action, as applied to Lichty's[1] experiments on the speed of esterification. Equivalent weights of ethyl alcohol and the several chlor-substituted acetic acids were made to react for definite intervals at 80°C. The alcohol, having been sealed in its own bulb, was placed in a tube containing the acid with a piece of glass rod, and the tube was then sealed. After heating in a glycerine bath to the required temperature, the bulb was broken by a blow from the rod. After a carefully timed interval, the reaction was stopped by immersing the tubes in water of about 15°C., and the free acid remaining was determined by ammonia, with rosolic acid. The work seems to be very well planned and successfully executed. From two to nine determinations were made for most of the intervals chosen, and the resulting means agree closely with smooth curves.

Numerical results are given in the tables which follow, showing variations in the calculated coefficients of speed. The course of the reaction is compared with that which would be expected for a reversible action, unmodified by secondary influences; and some hints are added regarding the secondary influence, which may necessitate an extension of present theories.

II. Mathematical Equations and Methods

1. *Fundamental formulas for mass action.*—Since we are dealing with a bimolecular reversible reaction, and equivalent weights of the active bodies, we must assume

$$\frac{dx}{dt}=k(a-x)^2-k'x^2; \qquad (1)$$

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[1] Am. Chem. Jour. 18, 590 (1896); Abstract in this JOURNAL 1, 67, (1896).

Where a=the quantitly of active substance taken;

x=the quantity that undergoes change in the time, t;

k=the coefficient of speed for the direct action;

k'=the coefficient of speed for the reverse action; and

$\frac{dx}{dt}$=the actual speed at any moment.

For convenience let k' be expressed as b^2k, and let $x=ay$. Then $dx=ady$, and

$$\frac{dy}{dt}=ak\left\{(1-y)^2-b^2y^2\right\}. \tag{2}$$

Let y_∞ express the limiting value of y, when the reverse reaction (between ether and water) exactly balances the direct one between alcohol and acid. When this condition is reached, $\frac{dx}{dt}=0$; hence, $(1-y_\infty)^2-b^2y_\infty{}^2=0$,

$$b=\frac{1-y_\infty}{y_\infty} \text{ and } y_\infty=\frac{1}{1+b}. \tag{3}$$

Equation (2) may also take the forms

$$\frac{dy}{dt}=ak\left\{1-(1+b)y\right\}\left\{1-(1-b)y\right\} \tag{4}$$

and
$$\frac{dy}{dt}=ak(1-b^2)\left\{\frac{1}{1+b}-y\right\}\left\{\frac{1}{1-b}-y\right\};$$

or, making
$$c=\frac{1}{1-b}=\frac{y_\infty}{2y_\infty-1}, \tag{5}$$

$$\frac{dy}{dt}=\frac{ak}{cy_\infty}(y_\infty-y)(c-y). \tag{6}$$

Eq. (4) is useful, when b is assumed to be a very simple number or fraction, so that y may be readily multiplied by its coefficients without the use of logarithms. Otherwise, eq. (6) is preferable.

2. *Integration.*—To integrate eq. (4), write

$$\frac{dy}{\{1-(1+b)y\}\{1-(1-b)y\}}=\frac{1}{2b}\left\{\frac{(1+b)dy}{1-(1-b)y}-\frac{(1-b)dy}{1-(1-b)y}\right\}=akdt$$

whence, by integration from zero,

$$\log_e\frac{1-(1-b)y}{1-(1+b)y}=2abkt;$$

or, writing *m* for the modulus of common logarithms,

$$log\frac{1-(1-b)y}{1-(1+b)y}=2abkmt. \qquad (7)$$

Also, between limits denoted by subscripts 1 and 2,

$$log\left\{\frac{1-(1+b)y_1}{1-(1+b)y_2}\cdot\frac{1-(1-b)y_2}{1-(1-b)y_1}\right\}=2abkm(t_2-t_1). \qquad (8)$$

If *b* is not a simple number or fraction, it is more convenient to integrate eq. (6) or to reduce (7) and (8), obtaining the following:

$$log\left\{\frac{c-y}{y_\infty-y}\,(2y_\infty-1)\right\}=2abkmt, \text{ and} \qquad (9)$$

$$log\left\{\frac{y_\infty-y_1}{y_\infty-y_2}\cdot\frac{c-y_2}{c-y_1}\right\}=2abkm(t_2-t_1)\cdot \qquad (10)$$

3. *Mode of using these equations.*—In the last four equations, the product *2abkm* has been assumed to be constant, and may be computed by dividing each time interval into the corresponding logarithm. If the series of resulting quotients proves to be nearly constant, the theory is confirmed, and *k* (the actual coefficient of speed in any convenient system of units) is found by substituting the proper value of *2abm*.[1] But if the series shows a marked increase or decrease, it is fair to conclude that the fundamental hypothesis is untrue, that we are not dealing simply with a bimolecular reversible reaction between equivalent masses, or (possibly) that we have assumed a false value for y_∞ and, therefore, for the related constant *b* or *c*.

In similar investigations, it has been usual to take the entire integral from zero, or from the first determination thereafter. Values for *2abkm* thus computed (multiplied for convenience by 10000) will be found in the tables, in the third column under each acid. When *k* proves to be a variable, it is better to use the integral between narrow limits, as the successive observations. A series of numbers is thus obtained, expressing mean values of the coefficient of speed

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[1] We may best express the value of *a* in gram-equivalents per liter, dividing the weight of one liter by the sum of the molecular weights. For this purpose it would be desirable to know the specific gravity of the various mixtures at the temperature of the experiment.

for short portions of the curve, and affording some insight into the nature of the perturbations with which we have to deal. See the fourth column under each acid, in the tables, where fluctuations in value are much more marked than in the third column. It is obvious that in many published investigations on the speed of chemical action (as with other dependent variables) where the fundamental equations receive a general confirmation by integration of a whole, it may be possible to detect many perturbations (and thus to modify or amplify the fundamental equations) by integrating between narrow limits, and studying such systematic variations as may then appear.

In case of frequent observations, the inevitable errors may accumulate so as to affect unduly the numbers derived from short intervals, accidental errors may obscure the perturbations; more regular results are then obtained by integrating for longer intervals, as from zero to the second observed point, from the first to the third, the second to the fourth, and so on. The table shows values thus obtained for trichloracetic acid.

Finally, if calculated values for k prove to be nearly constant for some portion of the curve, a mean for that portion may be obtained by selecting still wider limits, as illustrated in the tables.

III. Tables of Numerical Deductions

Lichty's mean results are repeated, for each acid, in the first two columns. Numbers proportional to the coefficient of speed, as obtained by integration from zero to each determination, are given in the third column; this being the usual method of testing such experiments. There is a marked diminution in the series; yet, since each number is (in a sense) a mean for the whole period from the beginning of the reaction, there is no clear indication of the changes. This is gained, however, by integrating between the limits of successive determinations, with results recorded in the fourth column, or those deduced for double intervals, as in the fifth column under trichloratic acid. These numbers are all calculated on the assumption of the limits assigned by Lichty himself; 68.65%, 71.22% and 74% for these three acids respectively. They show the same general features for each acid; *a steady decrease in the early* *stages is followed by a moderate increase, then by a rapid fall.* The minimum is most remarkable during the fifth minute for trichloracetic acid, as indicated by four pairs of determinations, published in Lichty's paper. The infinite value at the end of the series is a necessary result of the assumption that the result actually reached in experiment is the "limit" for indefinite time of action. The slight increase among the last few numbers could be made to disappear, by assuming a higher value for the limit.

MONOCHLORACETIC ACID Assumed limit, 68.65 per cent.				DICHLORACETIC ACID Assumed limit, 71.22 per cent.			
Lichty's determinations		$2abkm \times 10\,000$		Lichty's determinations		$2abkm \times 10000$	
t, minutes	y	From zero, by eq. (9)	For single intervals, by eq. (10)	t, minutes	y	From zero, by eq. (9)	For single intervals by eq. (10)
1	0.0178	72	72	1	0.0456	167	167[2]
3	.0509	71	70	3	.1133	149	140
5	.0765	66	58	5	.1648	139	123
10	.1338	61	57[1]	10	.2808	138	138
15	.1815	59	54	15	.3553	136	117
20	.2223	57	52	20	.4268	135	146
25	.2591	56	52	30	.4794	113	70
30	.2863	54	42	40	.5179	101	64
45	.3596	51	44	60	.5649	84	51
60	.4189	50	46	120	.6234	59	32
120	.5733	52	54	180	.6388	43	13
180	.6139	44	30	300	.6495	28	5
300	.6265	29	7	600	.6684	17	5
600	.6713	24	19	1200	.6773	9	2
870	.6745	18	3	1500	.6843	8	3
1440	.6748	11	0	3000	.6829	4	0
2520	.6782	7	1	4500	.7042	4	4
2880	.6812	7	5	6000	.7095	4	3
9420	.6865	∞	∞		.7122		

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[1] By integration between the limits for 10 and 120 minutes, the computed mean is 51.

[2] By integration between limits for 1 and 20 minutes, the computed mean is 133.

TRICHLORACETIC ACID

Assumed limit, 74 per cent.

Lichty's determinations		$2abkm \times 10000$		
t, minutes	y	From zero, by eq. (9)	For single intervals, by eq. (10)	For double intervals, by eq. (10)
1	0.0999	339	339	
2	.1540	278	217	278[1]
3	.1892	238	157	187
4	.2260	223	181	169
5	.2324	185	33	107
7	.2804	171	134	101
9	.3230	163	137	136
11	.3645	161	152	144
13	.3970	157	136	144
15	.4298	157	150	140
17	.4591	156	156	158
20	.4903	153	129	140
23	.5046	141	65	97
26	.5183	133	68	66
30	.5302	121	47	50
35	.5438	111	44	47
40	.5551	102	42	44
50	.5736	89	37	39
60	.5939	81	38	38
70	.6108	77	54	40
80	.6230	72	37	41
90	.6355	69	43	40
100	.6433	65	30	37
110	.6544	63	47	39
120	.6618	61	36	42
130	.6690	59	38	37
160	.6754	51	13	19
190	.6825	45	16	14
240	.6846	36	3	8
360	.7008	28	12	9
600	.7223	22	14	13

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[1] By integration between the limits for 2 and 20 minutes, the computed mean is 140.

IV. Possible Causes of the Variations

The following are among the various conditions which may be considered, in searching for disturbing influences :—

1. Is there some secondary chemical reaction? For example, does the water formed react upon the acid, generating HCl? Some attention has already been given, by the experimentors, to such contingencies.

2. With formation of ether, does the liquid separate into non-miscible layers? If the changing composition of such layers were determined, it would still be possible to construct a formula for the speed of action in each portion.

3. Does electrolytic dissociation affect the speed?[1] We may have one coefficient for the ions, and another for entire molecules, the observed speed resulting from both.

4. Does the reaction proceed to any considerable extent, after placing the tubes in cold water, owing to slowness in the cooling process? Such error in time measurements would chiefly affect the shorter periods; yet a constant error of this kind would be eliminated by using eq. (8) or (10), and omitting the first minute.

Further experiments are needed to determine the true cause. Among other phases of the investigation, parallel determinations may be made, under the same conditions of time and temperature, to compare the action of alcohol and acid with that of ether and water. This would at least afford valuable testimony in regard to the ratio, $k:k'$, and therefore of b, y_∞ and c. In many cases this work may be more trustworthy as well as more expeditious than the prolonged action required for direct determination of the limit.

V. Comparison of the Three Acids

The secondary influence must be more fully explained, before the actual constants can be determined, in order to trace the effect of successive atoms of chlorin in acetic acid.

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[1] Perhaps this hypothesis is the most probable. See Goldschmidt's discussion of "auto-catalysis", and Donnan's comment, in Ber. chem. Ges. Berlin, 29, 2208-2216, 2422-2423, which have appeared since this paper was written.

As Lichty points out, however, the percentages of mono- di- and trichloracetic acids esterified at 80° C. in one minute are the following :

1.78 : 4.56 : 9.99=1 : 2.56 : 5.61.

If we were justified in applying an extrapolation formula to find the percentage speeds at the very beginning, the first two determinations would yield the following :

1.82 : 4.95 : 12.28=1 : 2.7 : 6.7.

If we compute 20000*abkm* from the first minute's change in each case, we find the values :

72 : 167 : 339=1 : 2.3 : 4.7.

But if we select the middle portion of each curve, where *k* seems to vary comparatively little, the values of 20000*abkm* are

51 : 133 : 140=1 : 2.6 : 2.7.

Hence, dichloracetic acid reacts about two and one-half times as rapidly as monochloracetic ; but it is still uncertain what part of the higher curve should be taken as a suitable basis of comparison with the lower ones.

In conclusion, I wish to thank Mr. D. M. Lichty for the opportunity to discuss his interesting experimental results, and for friendly correspondence in regard to them.

Howard University, Washington, D. C.
September, 1896

PRECIPITATION OF SALTS

BY H. A. BATHRICK

It has been shown that the experiments of Gérardin[1] and of Bodländer[2] on the precipitation of salts from aqueous solution by alcohol can be represented by an equation of the form $(x+A)y^n=C$. where x and y denote respectively the quantities of alcohol and of salt in a constant quantity of water[3]. Though the agreement between the values calculated from the formulas and those found by direct measurement was satisfactory on the whole, there were discrepancies; especially in the solutions rich in alcohol. At the request of Mr. Bancroft I have made some measurements of the solubilities of several salts in aqueous alcohol of different strengths. As it is not easy to determine the amount of alcohol in the saturated solution directly I have avoided this by using aqueous alcohols of known percentage compositions by weight and working in closed vessels[4]. In this way all that was necessary for a complete analysis was to evaporate a weighed quantity of the solution to dryness and weigh the residue. The chief errors of this method are that the aqueous alcohol may change in composition by absorbing moisture or by dissolving solid matter from the glass bottles in which the mixtures are kept and that some of the liquid may evaporate before the solutions become saturated. The first difficulty is obviated by using bottles which have been thoroughly treated with steam; by making up relatively small quantities of each mixture so that it may not stand in the bottles very long; and by keeping the bottles carefully stoppered except when in use. In spite of these precautions

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[1] Ann. chim. phys. (4) **5**, 129 (1865).
[2] Zeit. phys. Chem. **7**, 308 (1891).
[3] Bancroft. Jour. Phys. Chem. **1**, 33 (1896).
[4] Cf. Nicol. Phil. Mag. (5) **31**, 374 (1891).

there are one or two cases where the large error shows that a change in the solution has taken place. It was not thought worth while to repeat these isolated experiments in order to get more accurate results. It must not be thought that this conclusion was drawn because the results did not agree with those calculated from the formula. That is, of course, not permissible. The conclusion was based on the fact that one or two observations when plotted did not lie on the empirical curve drawn through the points determined. It would have been a good plan to have tested the aqueous alcohol occasionally with the refractometer but this was not done. The second difficulty is not a serious one and can be eliminated by repeating the experiment. The mixtures of aqueous alcohol were put in carefully stoppered flasks together with a large excess of solid salt and the whole left twenty-four hours in an Ostwald thermostat. At the end of this time the solutions were analyzed by evaporation. Except in the case of ammonium chlorid, this determination is accurate to within one per cent. The values for the amount of salt in a gram of solution are probably accurate to within two milligrams. The values for salt in a hundred grams of water have, in addition, the error due to the composition of the aqueous alcohol, in most cases a very small one. I have made determinations at 30° and at 40° with aqueous alcohol and also two series with aqueous acetone at 40°. The results are given in Tables I–X. In the first column are the percentages by weight of water in the aqueous alcohol or aqueous acetone. In the second and third columns are the values for grams of salt in one gram of solution as calculated and as found. I have thought it better to tabulate the results in this form because these are the values given directly by analysis. The letters x and y in the formulas denote grams of alcohol and grams of salt in one gram of water, y in all cases referring to the salt. Where two formulas are given in one table, the second refers to the data below the dotted line.

The agreement is most satisfactory for all strengths of aqueous alcohol. The values of the exponential factors are the same that were used in describing the results of Bodländer and of Gérardin, confirming the assumption that this term is independent of the temperature. The agreement between the term A in my results and in those of Gérardin is not very good; but this is due to experimental error as he makes the solubility of potassium chlorid in pure water both at 30° and 40° about ten milligrams less per gram of solution than I have found it. I have made measurements of the solubilities in aqueous acetone only with potassium and sodium nitrates because the corresponding chlorids give two liquid phases at 40°. At a lit-

TABLE I

NH_4Cl at 30°

$(x+0.11)y^4=C \quad \log C=0.940-5$

$\%H_2O$	y calc.	y found	*log C*
100.00	0.291	0.288	0.879—5
91.72	0.256	0.261	0.990—5
83.10	0.227	0.241	0.151—4
74.05	0.212	0.216	0.006—4
65.58	0.177	0.178	0.947—5
54.13	0.145	0.145	0.950—5
45.67	0.121	0.123	0.006—4
34.96	0.092	0.088	0.692—5
24.39	0.062	0.060	0.850—5
12.05	0.028	0.028	0.893—5

TABLE II

NaCl at 30°

$(x+0.2)y^{1.5}=C_1 \quad \log C_1=0.320-3$

$(x+0.2)^{1.3}y=C_2 \quad \log C_2=0.945-2$

$\%H_2O$	y calc.	y found	*log C*
100.00	0.267	0.266	0.318—3
94.72	0.245	0.246	0.329—3
91.72	0.234	0.235	0.330—3
83.10	0.205	0.205	0.320—3
74.05	0.176	0.177	0.333—3
65.58	0.152	0.150	0.295—3
54.13	0.112	0.112	0.942—2
45.67	0.083	0.083	0.948—2
34.96	0.052	0.048	0.875—2
24.39	0.029	0.029	0.945—2
12.05	0.009	0.009	0.973—2

tle higher temperature the same phenomenon occurs with the two nitrates. It will be noticed that in changing from alcohol as a precipitating agent to acetone, the value of *n* changes; but the term due to the salt, namely *A*, remains unchanged. In spite of the fairly good agreement obtained in my results it does not follow at all that the values for *n* and *A* as given in the tables are in any sense

TABLE III

KCl at 30°

$(x+0.2)y^{2.5}=C_1$ $\log C_1=0.290-2$

$(x+0.2)y=C_2$ $\log C_2=0.350-1$

% H_2O	y calc.	y found	$\log C$
100.00	0.284	0.280	0.276—2
94.72	0.253	0.253	0.288—2
90.57	0.232	0.232	0.290—2
83.09	0.198	0.199	0.296—2
74.92	0.172	0.161	0.248—2
65.89	0.135	0.135	6.291—2
56.91	0.108	0.100	0.203—2
44.42	0.064	0.064	0.348—1
34.12	0.035	0.035	0.355—1
21.92	0.013	0.013	0.353—1
13.84	0.005	0.004	0.260—1

TABLE IV

KNO_3 at 30°

$(x+0.18)y^{1.4}=C$ $\log C=0.780-2$

% H_2O	y calc.	y found	$\log C$
100.00	0.315	0.313	0.776—2
91.72	0.237	0.244	0.798—2
83.10	0.182	0.183	0.786—2
74.05	0.135	0 131	0.758—2
65.58	0.102	0.102	0.781—2
54.13	0.067	0.065	0.762—2
45.67	0.047	0.043	0.725—2
34.96	0.027	0.026	0.745—2
24.39	0.013	0.013	0.746—2
12.05	0.004	0.004	0.742—2

absolute. By changing both *A* and *n* slightly it might be possible to obtain greater accuracy in the mathematical expression. At present we are unable to calculate any of the constants in the

TABLE V

NaCl at 40°

$(x+0.2)y^{1.5}=C_1 \quad \log C_1=0.345-3$

$(x+0.2)^{1.7}y=C_2 \quad \log C_2=0.080-1$

%H_2O	*y* calc.	*y* found	*log C*
100.00	0.269	0.269	0.343—3
94.72	0.248	0.249	0.356—3
92.05	0.238	0.239	0.360—3
83.18	0.208	0.205	0.318—3
73.54	0.177	0.177	0.349—3
64.91	0.151	0.151	0.345—3
55.46	0.125	0.124	0.323—3
45.71	0.098	0.093	0.040—1
34.75	0.061	0.062	0.097—1
25.95	0.038	0.038	0.098—1
10.35	0.008	0.011	0.311—1

TABLE VI

KCl at 40°

$(x+0.22)y^{3.5}=C_1 \quad \log C_1=0.400-2$

$(x+0.22)y=C_2 \quad \log C_2=0.430-1$

%H_2O	*y* calc.	*y* found	*log C*
100.00	0.296	0.295	0.396—2
94.72	0.267	0.264	0.389—2
90.57	0.245	0.250	0.426—2
83.09	0.211	0.216	0.429—2
74.92	0.178	0.179	0.404—2
65.89	0.146	0.147	0.414—2
56.91	0.116	0.116	0.398—2
44.42	0.075	0.076	0.434—1
34.12	0.041	0.039	0.412—1
21.92	0.015	0.016	0.428—1
13.84	0.006	0.005	0.323—1

formula and until we can do that, the constants as given in this paper can be considered only as first approximations. This inaccuracy does not interfere in any way with the conclusions drawn in regard to *n* and *A*. As long as the equation describing the facts remains of the same general form, the value for *A* will be a function of the solvent, the salt and the temperature and not of the precipitating agent, provided the concentrations are expressed in grams.

TABLE VII

KNO_3 at 40°

$(x+0.2)y^{\prime\prime}=C \quad log\ C=0.040-1$

$\%H_2O$	*y* calc.	*y* found	*log C*
100.00	0.396	0.392	0.034—1
94.72	0.340	0.340	0.040—1
91.74	0.313	0.320	0.055—1
83.04	0.245	0.250	0.053—1
74.46	0.192	0.194	0.046—1
65.01	0.143	0.143	0.039—1
55.99	0.104	0.104	0.036—1
45.05	0.068	0.067	0.039—1
34.91	0.041	0.042	0.049—1
23.55	0.020	0.020	0.047—1
11.55	0.005	0.006	0.139—1

TABLE VIII

$NaNO_3$ at 40°

$(x+0.6)y^{\prime}=C, \quad log\ C=0.820-1$

$\%H_2O$	*y* calc.	*y* found	*log C*
100.00	0.512	0.511	0.816—1
91.78	0.473	0.476	0.830—1
82.56	0.427	0.423	0.807—1
74.01	0.382	0.381	0.818—1
63.98	0.325	0.326	0.822—1
57.22	0.286	0.288	0.827—1
44.74	0.212	0.213	0.824—1
34.90	0.153	0.153	0.820—1
23.01	0.086	0.086	0.818—1
12.81	0.037	0.040	0.893—1

The value of *n* will also be independent of the temperature within the present limits. Nicol[1] has made some measurements on the solubilities of mixed salts using the chlorids and nitrates of sodium and potassium. His experiments were carried out at 20° while my

TABLE IX

Acetone : KNO_3 at 40°

$(x+0.2)y^2=C_1$ $\log C_1=0.960-2$

$(x+0.2)y=C_2$ $\log C_2=0.620-1$

%H_2O	*y* calc.	*y* found	*log C*
100.00	0.403	0.392	0.919—2
91.53	0.338	0.339	0.962—2
83.19	0.284	0.280	0.944—2
74.81	0.236	0.237	0.965—2
65.71	0.191	0.198	0.008—1
55.89	0.145	0.145	0.960—2
46.10	0.106	0.106	0.957—2
35.18	0.067	0.067	0.623—1
24.03	0.029	0.029	0.621—1
12.38	0.007	0.007	0.617—1

TABLE X

Acetone : $NaNO_3$ at 40°

$(x+0.6)y^3=C_1$ $\log C_1=0.830-1$

$(x+0.6)y'^2=C_2$ $\log C_2=0.170$

%H_2O	*y* calc.	*y* found	*log C*
100.00	0.511	0.511	0.835—1
91.53	0.477	0.477	0.831—1
83.19	0.440	0.439	0.823—1
74.81	0.402	0.399	0.815—1
65.71	0.357	0.367	0.888—1
55.89	0.306	0.316	0.894—1
46.10	0.251	0.247	0.804—1
35.18	0.187	0.187	0.169
24.03	0.099	0.098	0.161
12.38	0.030	0.031	0.173

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[1] Phil. Mag. (5) 31, 369 (1891).

determinations were made at 30° and at 40° so that the same constants can not be used in the two sets of experiments. By making a suitable correction for the difference in temperature it should be possible to calculate Nicol's data. The constant A in my experiments had the value of 0.2 for sodium chlorid at 30° and 40°. We shall not be far wrong if we assume the same value for 20°. The value of the same constant for potassium nitrate was 0.18 at 30° and 0.20 at 40° so that 0.16 seems a plausible value at 20° and, by the same reasoning, the most probable value of this constant for potassium chlorid is 0.18. With sodium nitrate, the question is a more difficult one as there are measurements only for 40°. Reducing this value in about the same ratio as in the other two cases we have 0.5 as the first approximation. Nicol's experiments have been calculated using these values and the results are given in Tables XI–XVI. The letters x and y denote grams of the salts in one hundred grams of water instead of one gram as in my own experiments so that the constant A is one hundred times the values first deduced. The general equation used has the form $(x+A)\,(y+B)^n=C$ as has been already pointed out by Bancroft.

TABLE XI

KCl at 20°

x = g. KCl y = g. KNO_3
in 100 g. H_2O.
$(x+16)^{10}(y+18)=C_1$
$\log C_1=52.350$

y	x calc.	x found
0.0	34.5	34.5
5.6	34.2	34.2
16.8	33.4	33.4
19.0	33.3	32.9

TABLE XII

KNO_3 at 20°

x = g. KCl y = g. KNO_3
in 100 g. H_2O.
$(x+16)\,(y+18)=C_2$
$\log C_2=7.950$

x	y calc.	y found
0.0	30.6	31.1
8.3	25.8	25.7
16.6	22.7	22.2
24.9	20.4	20.2
31.1	19.1	19.1
32.9	18.7	19.0

The agreement between the calculated and the found values is excellent when the common ion is the cation. The results of the precipitation of potassium chlorid by sodium chlorid are less satisfactory and it seems almost as if the variations were not due simply to experimental error. It is unsafe, however to base such a conclusion on the evidence now before us, more especially since the reverse precipitation can be expressed very accurately. Bodländer determined the solubility of potassium nitrate at 20.5° in solutions containing varying amounts of potassium chlorid and Bancroft has shown that these results can be described by the general formula for this case making use of the constants obtained from the precipitation of the same salts by alcohol. Since the limiting constant *A* n

TABLE XIII

NaCl at 20°

x = g. NaCl y = g. $NaNO_3$
in 100 g. H_2O
$(x+50)^{10}(y+20)=C_1$
$\log C_1=20.680$

y	x calc.	x found
0.0	36.7	35.9
14.2	32.2	32.8
28.3	29.4	29.8
42.5	27.4	26.9
54.5	24.9	26.0

TABLE XIV

$NaNO_3$ at 20°

x = g. NaCl y = g. $NaNO_3$
in 100 g. H_2O
$(x+50)(y+20)^{1.2}=C_2$
$\log C_2=4.137$

x	y calc.	y found
0.0	87.6	87.6
6.5	77.2	77.3
13.0	68.7	68.5
19.5	61.7	60.5
26.0	56.7	54.5

TABLE XV

NaCl at 20°

x = g. NaCl y = g. KCl
in 100 g. H_2O
$(x+18)^5(y+20)=C_1$
$\log C_1=9.970$

y	x calc.	x found
0.0	36.2	35.9
4.1	34.1	34.4
28.3	32.6	32.7
12.4	31.4	31.3
14.0	30.7	30.7

TABLE XVI

KCl at 20°

x = g. NaCl y = g. KCl
in 100 g. H_2O
$(x+18)(y+20)^{2.5}=C_2$
$\log C_2=5.600$

x	y calc.	y found
0.0	34.7	34.5
6.5	28.3	29.7
13.0	24.0	24.7
19.5	20.8	20.4
30.7	16.7	14.0

Bodländer's results was not the same as in mine, it has seemed worth while to tabulate this set of experiments using the same constants throughout that were used for the corresponding table in Nicol's experiments. This has been done and the results are given in Table XVII.

TABLE XVII

KNO_3 at 20.5°

x = g. KCl y = g. KNO_3
in 100 g. H_2O
$(x+16)(y+15)^4 = C_3$.

x	y calc.	y found
0.0	31.2	31.3
5.4	27.7	27.7
8.9	26.0	25.6
14.1	24.0	23.2
17.7	22.7	22.1
23.3	21.3	21.0
26.6	20.5	20.5
30.3	19.9	20.4

As will be seen, this formula describes the facts about as well as the slightly different one used by Bancroft. This brings out very clearly the difficulty in obtaining really accurate values for the so-called limiting constants A and B. The experimental error must be reduced far below its present value before one can hope to determine these values inside of ten per cent.

It will be noticed that two sets of equations are necessary to express the results when there are two salts in the solution. This will not surprise any one because one salt is solid phase in the system described by one equation and the other in the system described by the other equation and it has been clearly understood for ten years that the solubility curve has a break when there is a change in the nature of the solid phase in respect to which the solution is saturated. It is true that this has usually been applied to systems with two components where the temperature changes; but the two cases are analogous since both are monovariant systems[1]. There are also needed two equations to express the solubility of a salt in aqueous alcohol of varying strengths. The solid phase remains the same, but Bancroft has pointed out that the liquid phase does not and that there must be a sudden change at some point from water as solvent to alcohol as solvent. That this actually takes place can best be seen from a diagram. In Fig. 1 are the experimental data for the system, sodium chlorid, sodium nitrate and water at 20°, and for the system, sodium chlorid, alcohol and water at 30°. The abscissae are the logarithms of the grams of sodium chlorid in one hundred grams of water. The ordinates are logarithms of grams of sodium nitrate or grams of alcohol in one hundred grams of water. In order to keep the diagram within reasonable dimensions the scale for the alcohol concentrations is only one-half that of the sodium chlorid and sodium nitrate concentrations.

Along AB sodium chlorid is solid phase and along BC sodium nitrate, water being solvent along the whole length of the curve. There is a distinct break at B where the solute changes, in respect to which the solution is saturated. Along the whole of the curve $A_1B_1C_1$ sodium chlorid is solid phase; but there is a break at B_1 just as distinctly as at B. Since there is no change in the solid phase, there must be a change in the solvent to account for the break. Along A_1B_1 water is solvent and alcohol along BC.

There is still a word to be said about the expression for the precipitation of one salt by another: $(x+A)_1(y+B)^n=C$. Since two equations are needed, this involves six constants and it might well be urged that any one could devise two equations each with four constants which would represent ten observations with almost any required degree of accuracy. This is perfectly true; but the point is whether the equations used come under that head. The most conspicuous feature about the constants in a purely empirical formula is that they apply only to the cases for which they are deduced. This is not true here. The limiting constant *A* is the same whether the salt is precipitated by alcohol, by acetone or by another salt having

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[1] Prof. Trevor uses the terms nonvariant, monovariant and divariant to denote systems containing $n+2$, $n+1$ and n phases.

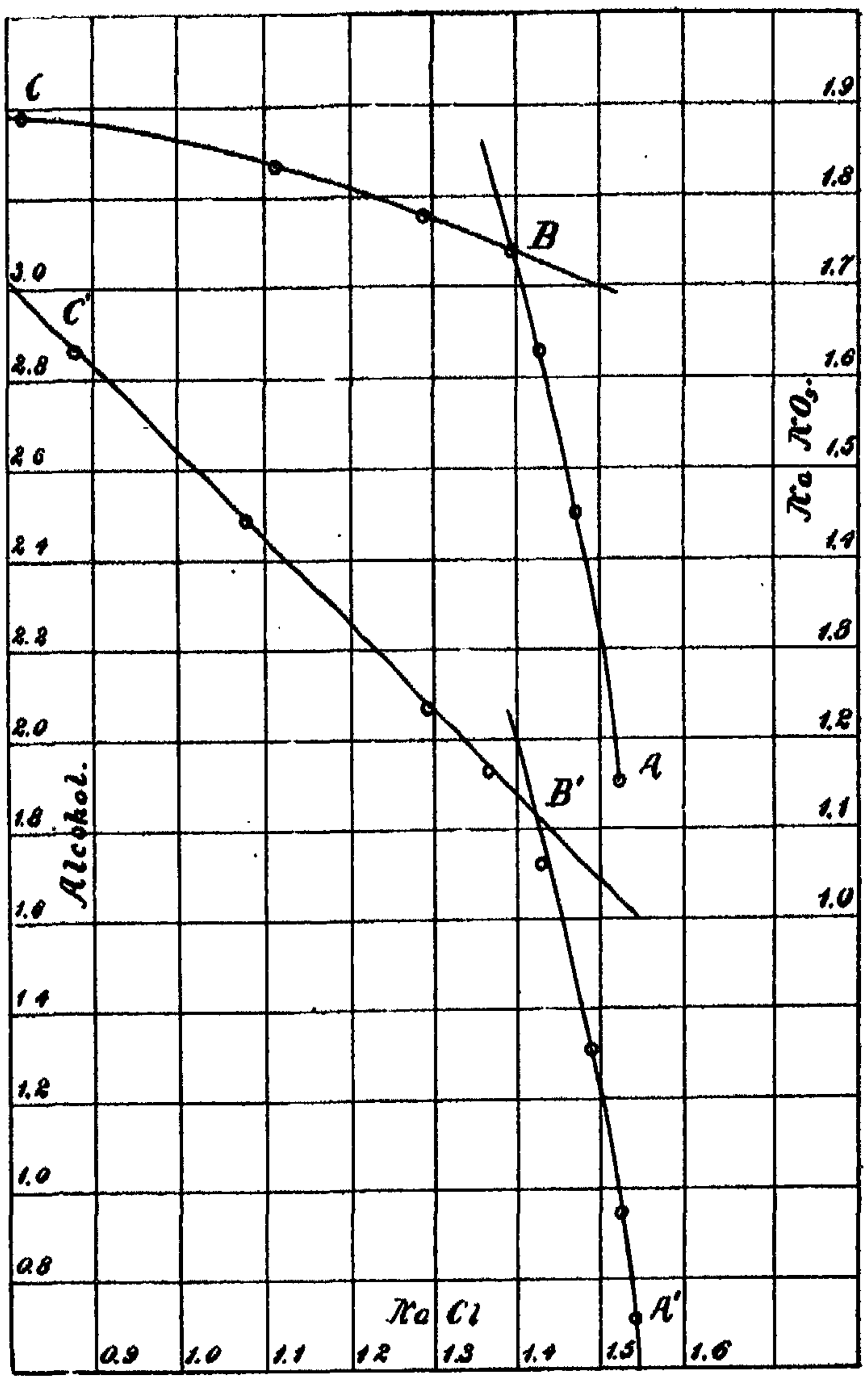
C
C'
B
B'
A
A'
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
Alcohol.
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1.0
Na NO3.
Na Cl
0.9
1.0
1.1
1.2
1.3
1.4
1.5
1.6

FIG. 1.

either the anion or the cation in common with the first. If we have determined the quantitative relations when the two salts are precipitated by alcohol, only one determination is needed to enable us to describe the way in which each of the salts will precipitate the other. The single determination is, of course, that of the solution saturated in respect to both salts. We can go further. If the exponential factor proves to be independent of the temperature, only one determination will be necessary in order to predict the mutual solubilities of two salts at all temperatures provided we have already studied the behavior of those salts in aqueous alcohol at the same temperature. In one sense the formulas used in the paper are empirical, because we cannot deduce them at present; but there seems to be no reason to suppose that they are really empirical which would mean that they could never be deduced. The exponential factors in the ordinary Mass Law applications would have been empirical if they had been discovered before Dalton's atomic theory had been promulgated and accepted.

The results of this investigation are :

1. The solubilities of salts in aqueous alcohol or acetone can be represented by the equation : $(x+A)y^n=C$, where y refers to the salt, x to the alcohol or acetone.

2. The factor n is apparently independent of the temperature.

3. The term A is a function of the salt, the solvent and the temperature.

4. It is not a function of x if x be expressed in grams.

4a. If x be expressed in reacting weights, the product of A into the reacting weight is independent of the nature of the substance denoted by x.

Harvard University; July 1, 1895.

NEW BOOKS.

Popular Scientific Lectures. *Ernst Mach: Translated by T. J. McCormack. 313 pages. The Relion of Science Library: The Open Court Publishing Co., Chicago, 1896. Price 35 cents.*—Of the lectures here set before us in English the first six are very popular indeed and seem to have been designed to give entertainment and perhaps amusement to mixed audiences. They certainly are lively and entertaining and have the additional advantage of being sound. They are not profound but they do not attempt, as is so often the case with popular lectures, to make the listener believe he has learned a great deal more than he has. The frequent allusions to the stylish dress, beautiful eyes and other charms of the ladies in the audience are deliciously German, though some of our ultra-serious women-students may find them a trifle frivolous. Opinions will differ on that as they do on the cleverness of the «Dolly Dialogues». Taken as a whole these are very good examples of the occasional popular-scientific lecture. The titles of the six lectures are: «The Forms of Liquids», «The Fibres of Corti», «On the Causes of Harmony», «The Velocity of Light», «Why has Man Two Eyes?» and «On Symmetry». The first gives an account of some of the phenomena of surface tension, and the fifth and sixth tell us something about binocular vision. The contents of the others are sufficiently indicated by the titles.

After these six lectures, which fill the first third of the book, come five more of a vastly higher order, delivered on occasions when the audiences to be expected were of a kind to appreciate something more serious than the six lectures referred to above. These five lectures are among the most scientific pieces of writing that the reviewer has ever read, and those who heard them delivered were privileged indeed. They show, if that were needed, that Professor Mach is one of the very few prominent physicists who are really scientific men in a wider sense than that implied by mere familiarity with laboratory work.

The first is «On the Fundamental Concepts of Electrostatics». It gives a clear account of the experimental basis of our ideas on the subject and some valuable criticism of the terms in which we usually embody those ideas. The second and perhaps the finest of these pieces is «On the Principle of the Conservation of Energy». It is certainly a splendid essay on the subject and deserves to be read many times by all who are interested in Physics. It contains an historical and critical discussion of the rise of the doctrine and of the earlier principles concerned in its development The six pages devoted to «Mechanical Physics» would, if physicists would only take to heart the obvious truths in them, do more good than the best *Lehrbuch* or *Handbuch* ever printed.

The next three lectures are on «The Economical Nature of Physical Inquiry», «Transformation and Adaptation in Scientific Thought» and «The Principle of Comparison in Physics». They are more philosophical than technical. The reviewer could not express his admiration for Professor Mach's manner of thinking as it is especially shown in those three lectures without using language which would seem much too hyperbolical for publication in a scientific journal; so he will content himself with having given the titles.

The twelfth and last of the whole series is an address «On Instruction in the Classics and the Sciences». It is a good piece of special pleading in favor of scientific education, but it seems to the reviewer that unless considered as directed against a very bad state of affairs the lecture is hardly fair to the opposing party.

The translator's work has been, on the whole, well done, though it is not perfect. In a number of places the translation seems faulty, though the reviewer, not having the German originals before him, cannot say definitely that it is. In some places the English is awkward and in at least one case it is very bad: at page 240, line 20 we have «the moon comports itself *like a heavy body does* with respect to the earth.» Nevertheless the translation is a good one. The book is a reprint of an earlier and more expensive edition. The printing is excellent and we owe thanks to the publishers for giving us so interesting a volume at so very low a price.

Edgar Buckingham.

Die Weisheit von der Welt-Kraft. Eine Dynamosophie. Mit einem Vorwort ueber die Rontgen-Strahlen. *Ferdinand Maack. Octavo, 68 pages. Otto Weber; Leipzig, 1897* (?) *Price, one mark.* Mr. Huxley says, in one of his essays, that he has learned to avoid all books in which the term «polarity» is used in any other than a specific, scientific sense ;—he who avails himself of Mr. Huxley's experience will lay aside the present brochure unread. The production is speculative writing of a not very dignified order and it is apparently, like much more of its kind, suggested by a very vague notion that natural processes tend to bring about a mutual equilibrium of the participating actions. But when a man undertakes to write a «dynamosophy», and sets out from ideas of an objective reality of force, there is little to be hoped for from his work. The prefatory reference to Röntgen's rays seems intended primarily for advertising purposes.

J. E. Trevor.

Theorie der doppelten Strahlenbrechung. *F. E. Neumann (1832). Ostwald's Klassiker der exakten Wissenschaften. No.* **76.** *52 pages. W. Engelmann. Leipzig, 1896. Price 0.80 marks.* **Zwei hydrodynamische Abhandlungen.** *H. Helmholtz (1858 and 1868). Klassiker. No.* **79.** *80 pages. Engelmann.* The present volumes of Ostwald's handy and very useful collection of famous scientific papers are edited by A. Wagnerin (Halle). The first of them is Neumann's earliest publication in theoretical physics, a paper which had an important bearing in the developement of optics; the problem solved was to deduce the laws of double refraction from mechanical principles. It is to be deplored that the editor has seen fit to interfere with the literary flavor of the original by modernizing the spelling of certain words.

The second of the little volumes is a reprint of Helmholtz's brilliant researches on vortex motion and on the production of currents within liquids. In the first it was shown that the so-called potential motion of liquids is characterized by the absence of rotation in the liquids, and in the second that the characteristic feature of the production of currents within liquids lies in the appearance of surfaces of discontinuity there. The chemical interest of these papers lies in their relation to W. Thomson's hypothesis of vortex atoms, which they suggested.

J. E. Trevor.

Der Dualismus in der Materie. *K. F. Wilby. Octavo, 111 pages. E. Speidel; Zürich, 1896. Price 2.60 marks.* After investigating «all processes of our total universe of phenomena»—something of a task one might think—the author of this little book has reached the conviction that they consist of the interaction of two ultimate quantities, which turn out to be oxygen (O) and hydrogen (H). The object of the volume seems then to be to develop the bearing of this insight upon the phenomena of light, of the solar system, of atmospheric currents, earthquakes, heat, color and so on; the author's classification is rather unusual.

It is so difficult to take the book seriously that a few passages are here appended to characterize its style: «Light is a very violent conflict between O and H» (page 8); «Mercury and Venus reflect sunlight pretty much as they receive it, they must therefore be very old and are probably crystallized». (page 14); «Water is presumably H_2O only at 4°; it becomes HO at the freezing point, its volume increasing because more O is taken up than H is lost, *etc.*» (page 84); and passages as amusing as the following are encountered: «The assumption that all optical phenomena consist of vibrations of an ether is groundless. An ether would certainly not vibrate with itself billions of times per second with any especial gratification, nor would it voluntarily make gradations therein to produce colors for the joy of mankind. All is contest, but motion like this is contest *in hoher Potenz!*» (page 89). Our author must be classed with the people who still contend that the earth is flat.

J. E. Trevor.

Grundriss einer Geschichte der Naturwissenschaften. *Friedrich Dannemann. Vol. I. Large octavo, xii and 375 pages. Wilhelm Engelmann; Leipzig, 1896. Price 6 marks, bound 7.20 marks.* There can be little doubt that the best way of studying science lies in reading the original publications of the men to whom the results of science are due. To fully comprehend the bearing of discoveries and to appreciate the insight which led to them one must understand the way in which they were made. Recognition of this fact is rapidly spreading, as is shown by the numerous recent reprints of classical papers in the field of physical science and by the growing habit of writing special treatises with the use of the historical method.

The present Outline of a History of Natural Science is an interesting attempt to widen the range of application of the historical method, in presenting, primarily for the use of high school pupils, a series of brief extracts from the writings of those who have contributed most to our knowledge of matters of fact. None of these selections are difficult to read, and they all bring the fine inspiration of great thoughts at first hand. The matters treated range through the period from the time of Aristotle to our own day, and in their sixty-two numbers they touch upon most of the epoch-making progress in natural history, physics, astronomy and chemistry. The choice of material is excellent and too much has been offered in no case, the collection is as admirable for what it omits as for what it includes. The chronological arrangement adopted is eminently sensible, and where translation has been necessary it has been clearly and smoothly done. Information of the kind presented should be a part of every one's education in this age of the world, and he who gains it gains an absorbing interest in seeing how the present generation has come by its heritage of the might, majesty, dominion and power of scientific knowledge.

Although the volume before us has been written for school children it can be read with an unusual degree of pleasure and profit by their elders. It may indeed be said that if the book had been arranged solely for an older audience its selections should have been made less brief, old forms of spelling should not have been replaced by new ones, and, possibly, many of the articles would have been better left in the languages in which they were first written. As it is, however, these objections do not apply, the work is admirably adapted to the purpose it is designed to fulfil. The author, or rather the translator and compiler, promises a companion volume, designed to throw light upon the mutual relations of the various steps in the historical development of our knowledge of nature; its appearance will be awaited with a real interest. *J. E. Trevor.*

The Universal Law of the Affinities of Atoms. *J. H. Loader. 93 pages. Chapman and Hall, Ld. London, 1896.* The argument of this book is what its author considers an example of scientific induction, an induction of *causes* from results—a method which is certainly not that of orthodox science. All science is taken to be a theory of a universal affinity of atoms; it is approached through contemplation of gravity, which is asserted to be «as at present understood, the outcome of the affinity of atoms». The introduction of atoms of ether, condensible to matter, and of calorific atoms which maintain fusion and «fused cohesion», supplies the working materials, and these things are employed to account for all astronomical, physical and biological phenomena—though the latter seem to call also for «animating organic atoms», which «are in their normal state when in ether».

The author is convinced of the value of his theory, but he presents it «with a certain amount of temerity and diffidence» in swerving from accepted precedent in the face of democratic indifference and of cultured conventionalism (page 7). The temerity is intelligible, but why the diffidence? Characteristic of the whole book is a hopeless unclearness of statement and an inability to confine the discussion to matters of fact. The English of its text, too, is the most astonishing the writer has ever seen, take as a sample the following, cut from a sentence on page 35: «When the pervading calorics gradually evolate, the combinations formed during calorific solution are detached and devolved, and unite spontaneously, culminating in various integrations and protoplastic formations,» etc. A good thing would be spoiled by this Latin dress.

J. E. Trevor.

Gesammelte Schriften von Eilhard Mitscherlich. *Herausgegeben von. A Mitscherlich. Large octavo viii and 668 pages. Ernst Seigfried Mittler und Sohn. Berlin. 1896. 15 marks.* The stately volume that lies before me contains a brief life of Mitscherlich by his son; many of his letters to his father, his brother-in-law and Berzelius; and his collected papers, some of which have not been published before. The close relations existing between Berzelius and Mitscherlich are well illustrated in the correspondence now presented to us and the selection is a good one though these letters are almost entirely upon subjects in which Mitscherlich was directly interested and others showing Mitscherlich's attitude towards Faraday's work might well have been included.

Mitscherlich's name recalls to every one the discovery of isomorphism; but that is in most minds all that it connotes. To such people it will be a revelation to read the papers on benzene and benzene derivatives; on the formation of ether; on chemical affinity; on the saccharimeter; on organic analysis; on the refractive index; on sulfur and on phosphorus. It is very interesting to notice that in 1828 Mitscherlich was perfectly clear about the solubilities of sodium sulfate in the neighborhood of 33°. The confusion which prevails in most text books even to the present day is therefore entirely unnecessary. To the chemist of to-day this volume of Mitscherlich's papers possesses more than a historical interest; the problems which are there brought to light are the problems of to-day. The study of solid solutions has only just begun; the question of passive resistances to change has not yet received any serious attention. The crystallization experiments with phosphorus may well form the starting point for a much modified view of chemical equilibrium, since the part played by sunlight in chemical reactions is far from being settled.

When one considers the extent of the field covered by Mitscherlich in his research work, one is inclined to ask where the same spirit still dwells. Not among the inorganic chemists for they know little of organic chemistry; not among the organic chemists for they care less about inorganic chemistry. It is only the physical chemist who is of necessity interested in the whole field and he is the legitimate successor of Berzelius, Mitscherlich, Gay-Lussac, Dumas, Liebig, Wöhler, Davy and Faraday. It was, therefore, strikingly appropriate that the speech at the unveiling of the monument to Mitscherlich should have been made by Ostwald.

Wilder D. Bancroft.

The Elements of Electrochemistry. *M. Le Blanc. Translated by W. R. Whitney. Small octavo, 277 pages. The Macmillan Co. New York, 1896. Price $1.50.* This book is an elementary treatise illustrating the application of the dissociation theory to electrochemical phenomena and the author has accomplished his task very successfully. The treatment is consistent throughout and while the reviewer feels that it is a mistake to ignore Helmholtz's work as has been done, that is a criticism of the plan adopted and not of the way in which it has been carried out. There are a few slips. The values in the table on page 144 are taken from an old paper of Jahn's and have since been corrected by him. Ostwald's formula for this single potential difference is declared wrong and very properly (page 228); but the student is left in the dark as to the reason for the change. It is comparatively simple to treat oxidation and reduction cells as analagous to gas cells when chlorin and hydrogen are taken as a typical case; but one would like to see this carried through with sodium bisulfit as the reducing agent. The explanation (page 214) of the working of the electrometer is not very satisfactory.

The book is a most useful one and this translation will prove of great service to many. While all students should be able to read German fluently, very few of them can. The translator has done his work well and he deserves especial thanks for having added an index.

Wilder D. Bancroft

Jahrbuch der Elektrochemie. *1895. W. Nernst and W. Borchers. Large 8vo. Vol. II. 280 pages. W. Knapp, Halle. 1896. 12 marks.* In this volume thirty-six pages are devoted to the scientific development of electrochemistry. The technical improvements are classified under the heads: voltaic cells; accumulators; electromagnetic separators; heating processes including welding; preparation of metalloids, metals and inorganic compounds including carbids, alkalies and chlorin; organic syntheses; bleaching and disinfecting, tanning and dyeing.

It is very satisfactory to find Nernst warning his readers against assuming that the problem of the voltaic cell is definitely solved. It is perfectly true, though not always admitted, that the recent development of electrochemistry starts from the molecular hypothesis and is not independent of it. The important features of the work of last year were the unexplained formula of Rudolphi and the discussion of the capillary electrical phenomena; both of these subjects are treated at some length in the present volume.

The part of the book devoted to technical processes contains a great deal of miscellaneous information, much of which is of little value. This is the fault of the people who patent imaginary improvements and the editor has called attention to the chaff as far as possible. To many, the treatment of the Borchers gas cell will seem a little disappointing. The matter is an important one and the present state of our knowledge might easily have been given in a few words.

Wilder D. Bancroft.

Recherches sur la congélation des solutions aqueuses étendues. *A. Ponsot. Large octavo. 114 pages. Gauthier-Villars; Paris, 1896.* After a review of the work already done in this special field, from which the author concludes that the «dissociation hypothesis of Arrhenius is not in accord with the experimental facts», the author gives an account of his own experimental and theoretical researches.

He first shows that when a dilute solution begins to freeze, only the pure solvent solidifies. As the freezing continues the temperature falls until it becomes constant at the temperature at which the «cryohydrate» is formed (Guthrie, 1875). The author shows that this so-called hydrate is nothing but a mechanical mixture of «ice» and «salt» crystals in definite proportions, and that the term Cryohydrate is thus misleading. He suggests the name *cryosel* instead.

This is the most valuable part of the experimental work, and it is to be regretted that he passes over it with so slight a description. The larger part of the book is given up to his work on the freezing point of dilute aqueous solutions. His method differs in no essential feature from that used by Nernst and Abegg[1]. The mechanical details are most ingeniously worked out. It is a matter of regret that with so careful attention to many irrelevant matters, as for example the exact verticality of the thermometer, he should have failed apparently to give any attention to the elimination of the «personal bias» factor. Could anything be so fatal to the exact measurement of the zero point of a fine thermometer as the fact that

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[1] Nernst and Abegg. Zeit. phys. Chem. **15**, 681 (1894).

the observer should permit himself to reject any unexpected observation on the ground that the water used in obtaining it was probably impure by reason of the difficulty in completely rinsing out the freezing tube? he tells us definitely, page 32, that his usual procedure is to continue making successive determinations of the zero point with new portions of water until he obtains two observations which *agree*.

It is to be regretted that he does not give us some of these daily series of successive observations, and that he fails, also, to give the zero points of his thermometer as observed on different days. This is a most important matter, and until the exact amount of variation in these observed zero points is known, we are altogether unprepared to judge of the accuracy of the measurements. In the meantime, we are certainly not ready to accept as final the most surprising of all his results, namely that the freezing point of water is lowered by the air which is dissolved in it. The maximum depression due to this cause, which he has observed is 0.0006° C. Since the only series of measurements in which he gives the values of the depressions to the ten thousandth of a degree are the three parallel series with sodium chlorid; and since these series disagree, on the average, almost 0.002° C., we are forced to believe that the author's conclusion about the influence of the dissolved air on the freezing point of water is without sufficient experimental basis.

Turning to the measurements on solutions, we are, perhaps, not surprised to find some unexpected results. He has studied KCl, NaCl, KBr, $BaCl_2$, $CaCl_2$, K_2SO_4 H_2SO_4, $Pb(NO_3)_2$, cane sugar, acetic and oxalic Acids. For the first three in very dilute solution, he finds that «The depression of the freezing point is proportional to the weight of salt dissolved in a given weight of the solution.» Since he examined no solutions of KCl and KBr, more dilute than 2/100 normal and 4/100 normal, respectively, one finds it difficult to understand why he uses the words «very dilute»; or why he should venture, by such extreme extrapolation, to assert anything about the behavior of these compounds in a state of dilution which he has not at all investigated. For $BaCl_2$, $CaCl_2$, K_2SO_4, and H_2SO_4, on the contrary, he finds no such proportionality. In fact, although he does not deem it worth while to call attention to the fact, the results for the dilute solutions of all these compounds *agree exactly* with the hypothesis of Arrhenius, within the limits of the experimental errors. The results for acetic acid permit no conclusion to be drawn in this respect. Those for oxalic acid are in marked discord with the Arrhenius hypothesis. The results for cane sugar show a uniform increase in the molecular depression as the concentration increases. The author explains this by assuming that the concentration of the solution is altered by the hydrostatic pressure of the solution itself. (?)

It should be added that he has shown great lack of care in the graphical representation of the results of other observers. For example, the curves which he draws to represent the Loomis results for cane sugar and sulphuric acid are so erroneous as to give no hint of the actual values.

The last sixty pages give the author's theoretical researches on the equilibrium phenomena of dilute solutions, He deduces a relation between the vapor tensions of ice, and water; and, further, between the vapor-tension of ice, water and salt solutions. He has also deduced a general formula for the depression of the freezing point, of which the formula of Dieterici is shown to be a particular case. His other theoretical deductions relate to the osmotic pressures of solutions. Since the theoretical researches of the author rests so generally on assumptions which are as yet without any experimental basis, it is perhaps premature to say anything about their value. *E. H. Loomis.*

Humphry Davy, Poet and Philosopher. *T. E. Thorpe. Octavo, 240 pages. The Macmillan Company; New York, 1896. Price $1.25.* This book forms one of the Century Science Series edited by Sir Henry E. Roscoe and published by the Macmillans.

It is an extremely interesting account of the life and work of Sir Humphry Davy and one that will be read by chemists with especial interest on account of the discoveries in chemistry with which Davy's name is always associated. The isolation of the metals of the alkalies, the determination of the elementary nature of chlorin and that hydrochloric acid contained no oxygen, the work on nitrogen chlorid, fluorin and iodine, and last, but by no means least, the invention of the safety lamp are described in detail and extracts from Davy's letters and those of his friends are given where these have any bearing on the subject. His wonderfully successful lectures at the Royal Institution are described and the effect of these on his audiences is shown. His influence in developing that institution, making it what it is to-day, is also brought out.

Altogether the book is a very readable one as «the story of a life of fruitful endeavor and splendid achievement;—the record of one who, if not wholly good or truly noble, has left a track of greatness in his passage through the world.»

W. R. Orndorff.

The Elements of Physics. *E. L. Nichols and W. S. Franklin, Vol. II, Electricity and Magnetism. Octavo, ix and 272 pages. The Macmillan Company; New York, 1896. Price $1.50 net.* A notice of the very admirable Elements of Physics by Nichols and Franklin was printed in the November number of this Journal, page 104, upon the issue of its first volume; we have now to chronicle the appearance of the second volume of the three which are to constitute the set. This one, treating Electricity and Magnetism, has been prepared according to the same general plan pursued in the preparation of the first. The book contains a great number of pleasing features upon which comment might pleasurably and profitably be made, but the writer refrains for the reason that much of the subject matter falls rather beyond the immediate province of this Journal. This is, however, not true in general, for the topics of resistance and electromotive force, of electrolysis, and of thermoelectric currents, to which in all some forty-four pages are devoted, have distinctly a physico-chemical interest. The book is of course intended primarily for undergraduates, but it can be used with great profit by any one for gaining, with a minimum of effort, definite ideas of the physics of electrical and magnetic effects,—both as to the main phenomena concerned and as to the methods now used to describe and coordinate them. The appearance of the volume must be hailed with the same gratification that was aroused by its predecessor in the series, as a serious contribution towards a very important aim of college instruction—abolition of the absurd and difficult teaching and learning of general physics without using the means of the calculus.

The details of printing, arrangement and illustration are pleasing; all the same the reviewer deprecates the practice of the publishers in filling the closing pages of such a volume with advertisements of their other publications, even though such advertisements are as likely to be of service to many readers as the present ones probably are. The habit may be businesslike but it is not artistic. The text is supplemented by a serviceable index.

J. E. Trevor.

Handbuch der Physik. *Herausgegeben von A. Winkelmann (Jena). In 3 Bände, large octavo. 878, 1742 and 1138 pages. Eduard Trewendt; Breslau. Agents for America: Lemcke and Buechner, 812 Broadway, New York. Completed in 1896. Price: vol. I, $8.00 or $8.90; vol. II, part 1, $6.60 or $7.50; vol. II, part 2, $9.35 or $10.25; vol. III, part ,1 $5.00 or $5.90; vol. III, part 2, $6.00 or $6.90;—the two prices in each case include paper binding or half-morocco respectively.* Winkelmann's huge general treatise on physics was originally intended to be an encyclopaedia of this science, but because of the wide separation of closely related subjects which would have resulted from a lexicographic arrangement it was deemed best to cast the book into the form of a treatise and confine the alphabetizing to the Index.

In order to study the physics of chemical processes one must know something of the methods and status of the different departments of pure physics, and out of this necessity arises the need of the physical chemist for comprehensive works where such information can be found readily. A work of this kind is the one before us. It is issued nominally in three volumes, which are further broken by the publisher into five parts. Of these, vol. I is devoted to mechanics and sound; vol. II, parts 1 and 2, to light and heat respectively; vol. III, part 1, to electricity, and part 2, to magnetism. The work constitutes a total of over thirty-seven hundred large octavo pages.

From the fact that more than a dozen authors have participated in its preparation it is apparent that uniformity in the style and in the character of treatment are not to be looked for; but, then, if non-uniformity is excusable anywhere it is so in a work designed primarily for reference purposes. This treatise, by reason of its comprehensive character, its extended citations of original literature and its many tabulations of experimental data, will be of great service both for general reference and for the rapid working up of special subjects. Its character is much more that of a handbook of experimental physics than that of a treatise upon physical theory,—it leaves the element of theory a little in the background. The more immediate interest of the physical chemist centers undoubtedly in the volume on heat, but the others also are sure to be of service in their turn. On the whole the work is an important one and should be available for reference in every laboratory where experimental work in physical chemistry is carried on.

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 which bear upon any phase of Physical Chemistry.

Qualitative Equilibrium.

Osmotic Pressure. *J. H. Poynting. Phil. Mag.* [*5*], **42**, *289* (*1896*). Starting with the idea that osmotic pressure is «an extra pressure produced by the motion of the dissolved molecules» the author finds himself «surrounded by the difficulties of the dissociation hypothesis». He therefore tries to account for osmotic pressure in another way. By imagining a liquid to be really a solid which is continually breaking down and changing its internal structure the author reaches the conclusion that osmotic pressure, lowering of the freezing point, etc., may be explained by an association of solvent and solute. His reasoning is aided by several intermediate hypotheses which are so chosen as to make the result agree with known facts.

The difficulties of the «dissociation hypothesis» are most apparent to those who are most firmly attached to some other hypothesis. As a matter of fact the idea of electrolytic dissociation rests on a basis exactly like that of gaseous dissociation. In the latter case we know that under some conditions a gas undergoes a change which increases its pressure and alters some of its physical properties, such as color. In the former we know that a dissolved electrolyte undergoes a process which increases its osmotic pressure and changes its color, conductivity, etc. If the statement of these experimental results brings difficulties to the pseudoscientists who try to explain everything by means of molecules so much the worse for the pseudoscientists. To any one who regards facts as of the first importance to science this article of Professor Poynting's is pure rubbish. *E. Buckingham.*

An Alteration in the Shape of Measuring Flasks. *H. Biltz. Ber. chem. Ges. Berlin.* **29**, *2082* (*1896*). A bulb is blown in the neck of the flask, above the mark; this increases the volume of air in the flask and makes it easier to thoroughly mix the contents. A funnel must be used in filling. Warmbrunn and Quilitz in Berlin manufacture flasks of this model to measure one litre, 500, 200 and 100 cc. *W. L. M.*

On Sublimation in the Vacuum of a Crooke's Tube. *F. Krafft and H. Weilandt. Ber. chem. Ges. Berlin.* **29**, *2240* (*1896*). The experiments were carried out as in the case of the boiling point determinations [Ber. **29**, 1316 (1896)]. Nineteen new boiling and sublimation temperatures are given, a large proportion of the substances experimented on subliming below their melting points.

The paper contains an illustrated description of a modified form of v. Babo's air pump, which the authors have found serviceable in their work. *W. L. M.*

On Adsorption of Vapors. *W. Müller-Erzbach. Wied. Ann.* **58**, *736* (*1896*) *and* **28**, *684* (*1896*); *also Wien. Akad. Sitzungsber.* **98**, (*IIA*) *327* (*1889*). Beginning in 1885 Müller-Erzbach has published a series of papers on the adsorption of the vapors of water, carbon disulphide, benzene, tetrachlormethane, etc., by alumina, ferric oxide, cobaltic oxide and charcoal: as this work is not referred to in the chapter on adsorption in Ostwald's *Lehrbuch*, a fuller account than otherwise necessary will be given in this place.

The adsorptive power of several of the substances experimented with is very considerable, ferric oxide suitably prepared can take up 40 per cent of its weight of water at 14°C, or 35 per cent of carbon disulphide at 8°C; the author has determined the tensions of the vapors given off by mixtures of known composition, calculating them in the majority of cases from measurements of the rate of evaporation of the adsorbed substance [details and control experiments, *Sitzungsber.* 328]. A static method is described in *Wied. Ann.* **58**, *749* (*1896*).

The following ‹ interpretation › of the phenomena is put forward in the papers under review :

1. The adsorbed vapor does not penetrate into the interior of the adsorbing molecule : *because* if ferric oxide saturated with the vapor of carbon disulphide be mixed with water, the carbon disulphide separates in the form of large drops ;

2. consequently it forms a layer round the molecule, attracted to the latter by the « molecular forces » ;

3. the thickness of the layer, other circumstances equal, is proportional to the weight of vapor adsorbed ;

4. determination of the « strength of the adsorptive force » must therefore afford a means of measuring the space through which the molecular attraction can be exerted ; and of determining the law according to which the force of attraction depends on the distance from the attracting centre.

After trying and rejecting several other plans, the author has succeeded in inventing the following « completely new scale for measuring the force of adsorption ».

« If one imagine a unit weight of uncombined water to be cooled from a certain initial temperature, until by the loss of heat its vapor tension has become equal to that of the adsorbed water at the initial temperature, then from the difference in temperature may be calculated the number of units of heat which exert the same influence on the water as the adsorption does, and which consequently may be considered equivalent to the latter . . . as the adsorbed water must be considered to be solid, its specific heat must be set equal to that of ice, viz. 0.502 ».

The application of all this may perhaps best be gathered from an example. The vapor tension of a mixture of alumina with 16 per cent of its weight of water, was 8.19 mm at 15.9°C. The temperature at which pure water has a vapor tension of 8.19 mm is 8.4°C. Hence the « value of the force of adsorption in calories » is $(15.9-8.4)\times 0.502=3.8$ cal. The thickness e_1 of the film of adsorbed water may be set equal to 16 arbitrary units. In a second experiment the force was found to be 34.2 calories for a thickness e_2

of 5.4 units (*i. e.*, 5.4 % of water was adsorbed). If the force of attraction fall off with the *x-th* power of the distance, then

$$\left(\frac{c_1}{c_2}\right)^x = \frac{cal_2}{cal_1}$$

whence $x=2.0$. In all of the author's numerous experiments the value of x determined as above comes fairly close to 2, consequently «the strength of the molecular force varies inversely as the square of the distance . . . and we can trace the energy of an individual molecule as far, in proportion to its size, as the gravitation energy of the sun has been observed to extend (in attracting the planet Neptune)».

Readers not infatuated with molecular-theoretical speculations of this kind, may well wonder how calculations based on such arbitrary assumptions can lead to the discovery of any regularity whatever. The explanation lies in a well known property of the vapor tension curves for pure liquids, *viz.*: that the logarithms of small differences in the tension are proportional to the corresponding differences in temperature. Thus the quantities cal_1 and cal_2 in the equation above may by replaced by $log\ \pi_1$ and $log\ \pi_2$ (where π is the tension of the adsorbed water in terms of that of pure water at the same temperature) and the relation discovered by Müller-Erzbach may be reduced to the form

$$c^2 = K\ log\ \pi$$

or, for constant temperature,

$$c^2 = K\ log\ p + const.$$

(where c is the percentage of vapor adsorbed, p its vapor tension, and k a constant).

A recalculation of a few of the author's tables shows that his results may be expressed by this latter formula at least as well as by the use of the «calorific values». *W. L. M.*

On the Genesis of Dalton's Atomic Theory. *H. Debus. Phil. Mag.* [*5*] **42**, *350* (*1896*); *also Zeit phys. Chem.* **20**, *259* (*1896*). With the aid of liberal quotations from the writings of Dalton, Thomson, Avogadro and others, the author seeks to support the following version of the origin of Dalton's atomic theory.

Dalton had long been accustomed to explain the expansion, diffusion, solution, etc., of gases in a mechanical way, by means of the old atomic theory, just as Boyle did a hundred and twenty years before him; in 1801 in order to explain the existence of equilibrium in a mixture of gases, he adopted the hypothesis (now known as Avogadro's hypothesis).

$$\frac{\textit{molecular weight}}{\textit{specific gravity}} = \textit{constant}$$

For several years he was unable to put his conceptions to the test, as no independent method was known for the determination of molecular weights; but the desire to discover such a method made him, probably, very observant of all circumstances which could promote his wish. In September, 1803, with a view of determining the composition of the atmosphere, he experimented on the reaction between oxygen and nitric oxid, and found that they combine in the proportions of 1.7 to 1, or 3.4 to 1, according to circumstances. These observations originated in Dalton's mind the idea that the atoms combine chemically «only according to very small numbers, one atom of *A* with one, two or three of *B*»; and a month after the experiments with nitric oxid Dalton's note book contains the first list of atomic weights. In 1805 the logic of his own atomic theory caused its author to abandon the hypothesis («Avogadro's hypothesis») which had first led him to the determination of atomic weights and volumes.

On the strength of a work published in 1894 [*Ueber einige Fundamentalsätze der Chemie. Cassel, G. Klaunig*] Debus claims priority over Roscoe and Harden [*A New View of the Origin of Dalton's Atomic Theory. London, 1896, Macmillan*] in affirming that the atomic theory led Dalton to the discovery of the law of multiple proportions; and in rejecting the generally received opinion, that the experimental discovery of the law of multiple proportions caused him to assume that chemical combination consists in the approximation of atoms with definite and characteristic weights.

The present paper contains also a vigorous reply to the remarks made on Debus' work by Roscoe and Harden in the first chapter of their «*New View*». *W. L. M.*

On the Influence of Double Bonds, etc., on the Optical Properties of Liquids. *P. Walden. Zeit. phys. Chem.* **20**, *569* (*1896*) Measurements of the densities and optical rotation, refraction, and dispersion of the (liquid) *l*-amyl ethers of sixteen acids :—four of the acetic and acrylic series, five of the succinic and fumaric series, tricarballylic and aconitic, hydrocinnamic cinnamic and phenylpropiolic, α- and β- naphtoic acids.

The author finds that

1. The replacement of a single by a double bond results in an increase in the specific gravity, an abnormal increase in the molecular refraction, and a marked increase in the molecular dispersion and optical rotation.

2. The optical effect of the treble bond is similar to but less than that of the double bond.

3. The naphtoic acids exhibit abnormality in refraction, dispersion and rotation.

4. Traube's method of calculating the molecular volume gives good results. *W. L. M.*

The Influence of the Temperature of the Freezing Mixture on Cryoscopic Measurements. *F. M. Raoult. Zeit. phys. Chem.* **20**, *601* (*1896*) *; also A. Ponsot. Bull. Soc. Chim. Paris.* (*3*) **15**, *1073* (*1896*). In determining the freezing points of solutions (*e.g.* in molecular weight determinations) it is customary to proceed as follows : The vessel containing the solution and a suitable stirring apparatus is placed in a freezing-mixture ; when the temperature has fallen a little below the freezing point of the solution a fragment of ice is added, whereupon the solution freezes, *i. e.* ice separates and the temperature rises by reason of the liberation of the latent heat of ice. The thermometer is closely watched and the maximum temperature noted as the « freezing point ».

This maximum temperature t_i is reached when in a unit of time the heat lost by radiation to the freezing mixture is equal to that liberated by the formation of ice together with that generated by the friction of the stirring apparatus ; it is evidently lower than the true freezing point t_o at which the solution and the ice are in equilibrium, and depends among other things on the *rate* at which ice is being formed—this in its turn is an unknown function of the concentration of the solution.

The problem, from the observed freezingpoint t_1 to determine the real freezing point t_0 has been attacked by Nernst and Abegg [*Zeit. phys. Chem. 15*, *681* (*1894*)] and more recently by Raoult; the latter obtains what he considers to be the true freezing point, by means of a graphic construction, from determinations of the various apparent freezing points of the same solution in freezing mixtures of different temperatures. He finds that, for solutions of the same substance but of different concentrations, the difference $t_0—t_1$ is proportional to the concentrations and thus in general to the «depression of the freezing point of the solvent» and concludes that the laws connecting the freezing point of the solution with its concentration are the same for the *apparent* as for the *true* freezing points—provided only that the former are all determined under strictly the same conditions.

To this Ponsot remarks:—1, that Raoult in his experiments has not paid sufficient attention to variations in the amount of heat generated by his stirring apparatus; 2, that his empirically discovered law connecting $t_0—t_1$ with the concentration is open to serious objection; 3, that some of Raoult's own results can best be explained by assuming errors in his calculation of $t_0—t_1$; and, lastly, suggests 4, that all necessity for this correction be avoided in the future by the use of freezing mixtures giving as near as may be the exact temperature of the freezing point to be determined.

W. L. M.

Boric Acid and its Salts. *Louis Kahlenberg and Oswald Schreiner. Zeit. phys. Chem.* **22**, *547* (*1896*). Aqueous solutions of boric acid, H_3BO_3, metaboric acid, H_2BO_2, and pyroboric acid, $H_2B_4O_7$, as well as aqueous solutions of their sodium salts, were examined cryosocopically and electrically. The results were:—

1. Only one acid, H_3BO_3, exists in aqueous solutions, the other acids combine with the water to form H_3BO_3.

2. An aqueous solution of borax is identical with that resulting from the solution of equivalent quantities of boric acid and sodium hydroxid.

3. In concentrated aqueous solutions of borax, the cation is sodium and the anion is an ion containing two atoms of boron.

The anions decompose hydrolytically on dilution, so that in a dilute solution the anion contains only one boron atom. Besides the ions, there are undecomposed molecules of H_3BO_3.

4. A solution of sodium metaborate is identical with a solution of equivalent quantities of boric acid and sodium hydroxid, or the proper quantity of borax and sodium hydroxid. The solutions contain few hydroxyl ions and therefore the salt is but slightly decomposed by water. A larger proportion of sodium hydroxid than one molecule to one molecule of acid, H_3BO_3, causes but slightly increased combination since the excess of hydroxyl ions is already in the solution.

Aqueous solutions of boric acid with glycol, glycerol, erythrite and mannite, as well as borax with the same alcohols, were also examined cryoscopically and electrically. The result showed that the alcohol combined with the boric ion when the solutions were concentrated; the complex ion decomposed on dilution. Four molecules of mannite to one of borax changed the alkaline reactions of borax to acid reactions. Ten molecules of erythrite and thirty of glycerol were required to produce the same effect.

C. L. S.

On Magnetic Rotary Power, especially of Aromatic Compounds. *W. H. Perkin. Jour. Chem. Soc.* 69, *1025* (*1896.*) An essay of over 230 pages. It embraces a review of all the work done in this field up to the present. The paper is full of experimental data and too long for useful abstraction other than some quotations from the conclusion.

" . . . There is a great difference between the rotation of aromatic and fatty compounds, the effect of the nuclei contained in them greatly influencing their rotation character.

"It is found that in many cases the substances behave like double molecules, the part containing the fatty groups acting like a fatty compound when it is thoroughly screened off from the phenyl by carbonyl, whilst that containing the nucleus acts in a different manner. . . When the screening is not perfect, as when effected by CH_2, the fatty groups retain the general character of their rotation, and although augmented to some effect, they are not affected nearly as much as when in direct union with the nucleus.

«The nucleus is also influenced by the groups and haloids it is associated with, thus with NO_2 and fluorin its influence is very greatly reduced, and it is also reduced, but not to so great an extent, by CO and by chlorin; it is worth noticing that all these are strongly electronegative. On the other hand, it is increased by association with hydrocarbon groups, especially when unsaturated, and greatly so by the electropositive group, NH_2 and its methylated and phenylated derivatives. It is seen, therefore, that strongly electronegative elements and groups act differently and in an opposite manner to the electropositive group. With bromin, however, little or no change occurs, and with iodin a slight increase takes place.

« . . In naphthalene both nuclei are apparently equally affected by the introduction of NO_2 or NH_2 although the displacement takes place in one only . . . in these and many other instances one is led to believe that, in these compounds, there is a kind of inductive effect from one carbon group to another, the influence of some of the groups approximating to the ordinary values found in the fatty series being multiplied by the number of carbon atoms in the nuclei ».

The paper contains a large number of useful data, such as melting points, boiling points, and specific gravities, in addition to the rotatory powers. *C. L. S.*

On the Hydrates of Alcohol. *H. P. Barendrecht. Zeit. phys. Chem.* **20**, *234*, *(1896)*. The author discusses the previous researches on this subject, with no reference however to Guthrie's measurements, and makes some experiments of his own to determine the nature of the crystals which separate from mixtures of alcohol and water. From seventy-five per cent alcohol there separate regular crystals which were at first supposed to be those of a new hydrate. On further investigation it appeared that these crystals were a second modification of ice. The same crystals were obtained from mixtures of water with different alcohols and with aldehyde. The author concludes that no hydrate of alcohol is known in the solid form.

W. D. B.

On the Density of Hydrogen. *E. W. Morley. Zeit. phys. Chem.* **20**, *242* *(1896)*. This is a translation of a paper which has already appeared in the «Smithsonian Contributions to Knowledge, 1895». The author made two series of the determinations of the density of hydrogen by the ordinary method; but rejects these owing to the possibility of mercury vapor having introduced a constant error. In the third, fourth and fifth series the hydrogen was weighed before passing into the flask in which its pressure and temperature were determined. This was done by absorbing the hydrogen in palladium, driving it out afterwards by heat. The advantage in this is that the ratio of the weight of the apparatus to that of the hydrogen is not so enormous as in the other methods and that the hydrogen comes in contact with mercury only after having been weighed. The mean value of the last three series gives for the density of hydrogen under normal pressure and temperature at the sea level and a latitude of 45° : D = 0.089873 g±0.0000027 g. *W. D B.*

On the Volumetric Composition of Water. *E. W. Morley. Zeit. phys. Chem.* **20**, *417 (1896)*. It was found impossible to decompose water electrolytically so that the gases formed were exactly in the proportion in which they recombine to make water. At temperatures above 20° there seems always to be an excess of oxygen. The author's measurements were made at 0° and hydrogen was always in excess. Theoretically there should be some intermediate temperature where neither gas would be in excess; but the equilibrium is not a function of the temperature only. After making all corrections the author finds, for the ratio of the volumes in which oxygen and hydrogen combine, the number 2.00269. This coincides very closely with the values obtained by Scott and by Leduc. Since the best determinations of the ratio of the densities of oxygen and hydrogen give 15.90 for the final result, the atomic weight of oxygen becomes by this method, 15.879. The synthesis of water from weighed quantities of oxygen and hydrogen gave for the ratio of the weights the figure 15.879, the exact value obtained by the other method. It seems safe to consider this value as accurate to 1/10000 unless some flaw is discovered which affects all determinations of this sort. For anyone who is interested in the making of exact measurements this investigation will always be a classic. It is almost pathetic to read the trials which the author has gone through. *W. D. B.*

On Numerical Relations among the Atomic Weights of the Elements. *M. C. Lea. Zeit. anorg. Chem.* **12**, *249* (*1896*). The differences in the atomic weights of two successive elements are about 16 or about 45 or about 88. This applies to all elements except those which have only colored ions. From the behavior of sodium gold chlorid the author concludes that gold can form colorless ions. It is thus clear that the word ion is used in a different sense from the usual one. *W. D. B.*

The Color of the Alcohols compared with the Color of Water. *W. Spring. Zeit. anorg. Chem.* **12**, *253* (*1896*). In a tube twenty-six meters long water has a deep blue color, methyl alcohol a greenish blue color, ethyl alcohol a somewhat similar color while amyl alcohol is greenish yellow. Ligroin gives a deep yellow color under the same circumstances. *W. D. B.*

On Compounds of the lower Oxids and Sulfids of Molybdenum with Ammonia and Potassium Cyanid. *K. van der Heide and K. A. Hofmann. Zeit. anorg. Chem.* **12**, *277* (*1896*). The authors have prepared and described the compounds $4MoO_3.MoO_2.2NH_3.7H_2O$; $MoO_2.4KCN.NH_2OH.H_2O$; $MoO_2.4KCN.10H_2O$; $Mo_2S_3.6KCN.5H_2O$; $MoO_2SO(CN)_2.4KCN.4H_2O$; $Mo_3S_4(CN)_3.5KCN.7H_2O$. None of these substances were investigated from the physico-chemical point of view in spite of the fact that there are reasons (cf. page 287) for suspecting the existence of solid solutions.

W. D. B.

On the Reactions occurring in the cold between Phosphoric Acid and Ether in presence of Water. *M. Berthelot and G. André. Comptes rendus*, **123**, *344*, (*1896*). If a little phosphoric acid be added to a mixture of water and ether the ratio of the concentrations is 2900 : 1, the aqueous solution being the more concentrated. With increasing amounts of phosphoric acid the ratio decreases until there is but one solution phase. This is accounted for by the assumption of instable compounds of phosphoric acid and ether though it is clearly a case of two partially miscible liquids dissolved in a third in which both are soluble. It is a question whether this characteristically French explanation is worse than the German method of ignoring concentrated solutions entirely. *W. D. B.*

On the Volatilization of some Refractory Substances, *H. Moissan. Ann. chim. phys.* (7) **9**, *133* (*1896*). Qualitative experiments on the volatilization of metals, metalloids and the oxids of calcium, magnesium, zirconium and silicon at the temperature of the electric furnace. Only silver and the oxids of zirconium and silicon boil below this temperature. Manganese volatilizes with extraordinary rapidity but the reason for this is not clear from the data given.

W. D. B.

Researches on Nickel Cyanid. *R. Varet. Bull. Soc. Chim. Paris*, **15**, *1081*; **On the Salts of Mercury which contain Oxygen.** *Same 1084*, (*1896*). Thermochemical data, with appended comment.

J. E. T.

The Chemical Inactivity of Röntgen Rays. *H. B. Dixon and H. B. Baker. Jour. Chem. Soc.* **59**, *1308* (*1896*). Röntgen rays do not affect the chemical combination of mixtures of CO and O_2 (dry or moist), H_2 and O_2, CO and Cl_2, H_2 and Cl_2, H_2 and SO_2 (dry), nor the chemical state of solutions of sodium sulfit, nor that of H_2O_2, nor the glowing of phosphorus. *J. E. T.*

Preparation and Properties of Titanium. *H. Moissan. Ann. chim. phys.* (7) **10**, *229* (*1896*). This article has a purely inorganic-chemical interest, save for the statement that cast titanium is the most refractory body which has yet been obtained in the electric furnace; it is more infusible than vanadium and it leaves such metals as chromium, tungsten, *etc.* far behind in this respect. Its preparation required the employment of a one hundred horse power dynamo. *J. E. T.*

An Empirical Relation between Melting-Points and Critical Temperature. *F. W. Clarke. Am. Chem. Jour.* **18**, *618* (*1896*). The author has calculated the ratio of the critical temperature to the freezing temperature, on the thermodynamic scale, for about thirty substances. For nine of them this ratio has the fairly constant value 2, for cyanogen and three oxids of nitrogen it is near 1.7, for five benzene compounds it lies near 2.8, and so on. It ranges mostly between 1.6 and 3.0, though yet wider variations are observed; the author is impressed nevertheless by the apparent agreement in some cases. *J. E. T.*

Position-Isomerism and Optical Activity; the Methylic and Ethylic Salts of o-, m- and p- Ditoluyltartaric Acids. *Percy Frankland and Frederick Malcolm Wharton. Jour. Chem. Soc.* **69**, *1309 (1896).* The investigation was to determine the effect of position isomerism upon the optical activity of a benzene compound. Also the effect of temperature. Series of measurements at differing temperatures were made with the ortho, meta and para-ditoluyltartrates of both ethyl and methyl. The results show that the *o*-arrangement has the least rotatory effect and the *p*-arrangement the greatest, the *m*-arrangement being between these two. This is in accordance with Guye's theory that the rotatory power of a group is dependent not only on its mass but also on the moment of the mass around the asymmetric carbon atom. *C. L. S.*

Quantitative Equilibrium.

On Some Cases of Unstable Equilibrium in Salt Solutions. *Ad. Blümcke. Zeit. phys. Chem.* **20**, *586 (1896).* In previous papers (Zeit. phys. Chem, **6**, **8**, **9** and **11**) the author has drawn a number of theoretical conclusions with regard to the forms of the isothermal surfaces for systems of two and three components. The coordinates used are *p*, *v* and the fraction of the whole mass formed by one of the components. The author starts with the assumption that beside the «empirical» isothermal line found during a change of state of a system containing one or more components there is also a «theoretical» isothermal of James Thomson's S-form and he investigates the geometrical relations of the «theoretical» and «empirical» isothermal surfaces.

The present paper is a continuation of two earlier ones (*Zeit. phys. Chem.* **9**, *323, 1892* and **11**, *645, 1893*). It describes experiments undertaken to show the existence of the unstable parts of the theoretical isothermals for systems of three components. The components used were (1) water, (2) sodium acetate or hyposulphite or calcium chlorid, (3) NaCl, NaBr, NaI, KCl, KBr, KI, NaH_2PO_4, $K_4Fe(CN)_6$, $K_3Fe(CN)_6$, $BaPt(CN)_4$, $CoCl_2$, PbI_2 or $K_2Cr_2O_7$. Various cases of unstable, undercooled liquid mixtures were found. The properties of these undercooled mixtures seemed not to differ from those of stable solutions (as was to be expected, of course). As none of the experiments are quantitative they do not enable us to find points on the unstable portions of the isothermals but merely show that such points exist. The author also describes an experiment with Bunsen's ice calorimeter where, apparently, ice existed for several hours in a state of equilibrium, but not in contact with water, at a temperature above the melting point for the given pressure. *E. Buckingham.*

The Viscosity of Liquids above their Boiling Points. *A. Heydweiller. Wied. Ann.* **59**, *193* (*1896*). The object of the experiments was to find how the viscosity varies with the temperature when the temperature approaches the critical point. The liquids were enclosed in sealed tubes with mercury and no air. The tubes were ring-shaped with one side capillary. By proper handling the liquid and the mercury were so arranged that the mercury by sinking on one side drove the liquid up before it on the other through the capillary. The rate of advance of the mercury meniscus in the vertical capillary was measured by the cathetometer. This rate together with the radius of the tube and the pressure permit the calculation of the coefficient of viscosity. The apparatus is described in an earlier paper. (*Wied. Ann.* **55**, *561*, *1895*.)

Various organic liquids were tried and no satisfactory formula was found for representing the results. For groups of similarly composed liquids the course of the viscosity changes is similar. Different groups behave differently. It appears that polymerisation shows in the viscosity as it does in the surface tension, but the data are not sufficient for the formulation of any rules in this regard.

E. Buckingham.

On the Measurement of Low Temperatures. *L. Holborn and W. Wien. Wied. Ann.* **59**, *213* (*1896*). The object of the experiments was the comparison with the hydrogen thermometer of pure platinum resistances and thermocouples of iron and constantan. The platinum resistances were enclosed in the bulb of the thermometer. The various samples of platinum wire did not act identically. The resistances could be expressed within one degree by a formula of the second degree, while the mean deviation was only a few tenths of a degree. Tables are given of the mean temperature coefficients for the various specimens for the temperatures 0° to +100°, 0° to −78°, −78° to −189° and 0° to −189°. The maximum difference between the values for different wires was somewhat less than one in twenty. Thermoelements of different samples of iron and constantan gave readings differing by as much as two degrees. Boiling air was used for producing the lowest temperatures (−189°).

In addition to the experiments mentioned several others were made on the boiling point and vapor pressure of (O_2+7.6 per cent N_2) and on the melting points of several organic substances which have distinct points of crystallization between −79° and −130°. The temperatures were here measured with the platinum resistances or the thermocouples. Finally a comparison of the hydrogen and the air thermometer shows that at −189° they agreed within 0.7°.

E. Buckingham.

The Mutual Relation of the Laws of Boyle, Gay-Lussac, Joule, etc. *G. Bakker. Zeit. phys. Chem.* **20**, *461* (*1896*). In an earlier paper (*Ibid* 17, 684) the author had shown that of the five laws:

1. Law of Joule, $\iota = -f_1(T)$;
2. Law of Boyle-van der Waals, $p(v-b) = f_2(T)$;
3. Law of Gay-Lussac, $v-b = TF(P)$;
4. Law that c_p and c_v are temperature-functions;
5. Law that $c_p - c_v = const$;

any one involves the remaining four if it be assumed that for low density or high temperature one may write

$$p(v-b) = RT.$$

Baynes (*Ibid* **18**, *335*) has attacked the paper upon the ground that its results require the assumption of a sixth law,—entirely overlooking the stated assumption upon which Bakker's conclusion was made to rest.

J. E. T.

Measure of a Heat of Esterification through the Action of an Acid Chlorid upon Sodium Alcoholate. *J. Cavalier, Bull. soc. chim.* **15**, *932* (*1896*). Indirect determination of the heat effect:

H_3PO_4 cryst. + $3C_2H_5OH$ liq. = $(C_2H_5)_3PO_4$ liq. + $3H_2O$ liq. − 9.4 Cal.

J. E. T.

A Method for Determining Specific Heats of Liquids at Temperatures up to 90°C. *A Schlamp. Wied. Ann.* **58**, *759* (*1896.*) The liquid (300–400 grams) whose specific heat was to be determined was placed in a cylindrical vessel of thin brass, warmed on a sand-bath to about 90°C and then suspended in a covered metal box kept at 90°–93°C by means of a steam bath. A current of 3.5 to 4.5 ampères was then passed for two or three minutes through a manganine wire resistance of 2.2 ohms suspended in the liquid, and the rise of temperature (4° to 7°C) measured by a Beckmann's thermometer divided into 1/50 degrees. The quantity of heat given off by the coil was determined in a parallel experiment in which the same current was employed to warm a liquid of known specific heat—water could not be used because of its conductivity. The liquid was stirred during the experiment and the usual corrections were made for the radiation, water value of the stirrer, etc., etc. Control experiments showed an error in same case of 0.5 per cent of the values obtained for the specific heats. The method promises to be of service in measuring variations in the specific heat with the temperature, and in obtaining the specific heat of substances which melt between 15°C and 96°C. *W. L. M.*

Velocities.

On the Catalytic Action of Acids on the Reaction of Etherification. *H. Goldschmidt. Ber. chem. Ges. Berlin.* **29**, *2209* (*1896*). In a previous paper [*Ber* **28**, *3218* (*1896*)] the author was led to the conclusion that the action of strong acids in promoting etherification is due to the presence of hydrogen ions. This view is now confirmed by experiments made on the etherification of phenylacetic acid by alcohol in the presence of picric acid as catalytic agent, which show that the rate of change is much diminished by addition of the neutral salt of picric acid with *p*-toluidine. Want of knowledge of the degree of dissociation in alcoholic solution of the picric acid and of its salts, prevents any quantitative prediction of the effect of the picrate.

A study of the etherification of trichloracetic acid dissolved in a large excess of alcohol without the addition of a catalytic agent, and a recalculation of Peterson's measurements on the etherification of formic acid, shows that both reactions are bimolecular; the author finds an explanation of this rather startling discovery in the catalytic action of the acids in question on their own etherification.

One important result of this work, which Goldschmidt does not fail to emphasize, is that it does away with the time-honored «explanations» of the action of strong acids in accelerating the process of etherification—such as references to their ‹powers of extracting water› or assumptions of otherwise unknown addition products, or (in the case of hydrochloric acid) of the intermediate formation of an acid chlorid, etc., etc. *W. L. M.*

Electrolysis of the Salts of Nonhydroxy-acids. *J. W. Walker. Jour. Am. Chem. Soc.* **69**, *1278* (*1896*). The author sought to prepare dihydric alcohols by electrolysis of the alkali salts of these acids (as glycolic and lactic) and of ethoxyacids; in accordance with Kolbe's synthesis of ethane from sodium acetate. Aldehydes were the chief organic products of electrolysis. A small quantity of hydrobenzoin was obtained by electrolysis of potassium mandelate; but whether it was formed directly

$$2C_6H_5CHOHCO_2K=C_6H_5(CHOH)_2C_6H_5+2CO_2+2K$$

or by reduction of benzaldehyd, was not determined. With other acids the results were negative. *R. B. W.*

On the Difference between Ethers and Salts, with special regard to the Constitution of Fuchsin. *Reply to Tortelli. A. Rosenstiehl. Bull. Soc. Chim. Paris.* **15**, *952–959* (*Aug. 1896*). It is generally admitted that salts readily enter into the reactions appropriate to the corresponding acids, while ethers do not. Tortelli (Gazz. chim. ital. **25**, 22 and Ber. chem. Ges. Berlin, **26**, 1702, 1704) rejects such formulas as $(H_2NC_6H_4)_3{=}C{-}Cl$, and regards the fuchsins as true salts, because of their ready precipitation by silver nitrate, etc., especially in presence of acid or alcohol. To this, Rosenstiehl replies:

1. Methyl iodid in aqueous solution, like sodium iodid, may be completely precipitated by silver nitrate. Ethyl bromid and triphenylchloromethane react still more quickly.

2. Some salts react as slowly as ethers; *e.g.*, the acetcchlorids of iron, the iodomethylates of triamidotriphenylmethane (in the cold) and Recoura's sulfates of chromium.

3. While rapid action is the rule with salts and the exception with ethers, the assumed difference is no longer distinctive; and it follows that Tortelli's experiments do not determine the constitution of the fuchsins.

With ethers (as the author claims) the metathesis with silver nitrate, etc., is certainly preceded by hydrolysis; with salts which undergo slow precipitation, the reaction occurs under the same conditions (water, time and heat) that produce hydrolysis of ethers,—the reaction proceeds as though hydrolysis must precede precipitation. But, see the next abstract. *R. B. W.*

On the Hydrolysis of Methyl Iodid. *A. Rosenstiehl. Bull. Soc. Chim. Paris.* **15**, *964* (*1896*). One *cm* of methyl iodid (2.18 grams) was dissolved in 160 *cm* of distilled water, and 2.87 grams of silver nitrate (1/10 excess) were then added. After certain intervals of time, at the temperature of the laboratory, the silver iodid was filtered off to be weighed, sodium chlorid was added to precipitate the silver, and the free acid was titrated in the filtrate.

The rapidity of hydrolysis is shown by the following results, the temperature being higher in the second series than in the first.

Time		CH_3I by estimation of iodin	CH_3I by acidimetry
0 h.	25 min.	1.023	
1	15		1.28
14		2.06	1.80
24		2.08	1.97
43		2.10	2.01
4		2.02	1.79
8		2.11	2.01
		Theory, 2.18	

In the absence of silver nitrate, only 0.014 grams were hydrolysed in 43 hours, 0.038 in twenty days, and 0.037 in fourteen days; hence methyl iodid is one of the most stable ethers, in aqueous solution.

It will be noted in the table, that the acid found is about 90 per cent to 95 per cent of the equivalent of silver iodid precipitated. According to the author's previous paper (page 955 of the same Bulletin) this shows that the chief reaction is not double decomposition between the salt and the ether, but first there is an hydrolysis of the ether, followed by the reaction

$$HI+AgNO_3=AgI+HNO_3.$$

The reviewer suggests that further proof is needed. Why may not the double decomposition take place first, followed by hydrolysis of ethyl nitrate. *R. B. W.*

Electrochemistry

Address before Section B of the American Association for the Advancement of Science. *By the Vice-President, C. L. Mees. Science* **4**, *507* (*1896*). To all intents and purposes, although not ostensibly, a review of the history of electrochemistry as given in Ostwald's *Elektrochemie*. It is a little striking to read (page 511) that the work of Helmholtz, Gibbs, *etc.*, on voltaic cells consisted in an application of the principle of the conservation of energy; and (page 516) that «Osmotic pressure seems to be simply a molecular kinetic effect». The names of many of the authorities cited are misspelled. American physicists are strongly urged by the author to take up the study of electrochemical problems.

J. E. T.

The Conductivity of Solutions of Acetylene in Water. *H. C. Jones. Am. Chem. Jour.* **18**, *623* (*1896*). Earlier work in conjunction with Allen (*Ibid* **18**, 375) had shown a relatively high electrical conductivity of aqueous solutions of acetylene which did not redden litmus. It was suspected that in the preparation-reaction between potassium cyanid and cuprous acetylid, ammonia might have resulted from the action, upon the excess of potassium cyanid, of the potassium hydroxid which was produced. So the acetylid was prepared free from ammonia, and the acetylene liberated from it by hydrochloric acid, solutions of the gas were then found to have but slight conductivity if any. Ammonia, however, could not be found on repeating the earlier work with especially pure material, so the author concludes that the acetylene first used contained a volatile impurity—probably ammonia. *J. E. T.*

On the Theory of Liquid Cells. *J. M. Lovén. Zeit. phys. Chem.* **20**, *593*, *(1896)*. A computation of the potential difference between two isosmotic solutions, one containing a monovalent cation with a monovalent anion, the other containing a bivalent cation with a monovalent anion. The substances were hydrochloric acid on the one hand, and barium, calcium, magnesium or zinc chlorid on the other. The solutions had to be isosmotic to get over mathematical difficulties. The equation for the potential difference between the two solutions was

$$\pi = 0.002T \frac{3u_1 - 2u_2 + v}{3u_1 - 4u_2 - v} \log \frac{3(u_1 + v)}{4(u_2 + v)}$$

where T is absolute temperature of measurement, u_1 the migration velocity of monovalent cation, u_2 that of bivalent cation, and v that of anion; *log* refers to Brigg's logarithms.

A few measurements are appended. When the concentration was 0.1 gram molecule per liter, the equation was unsatisfactory, but for 0.01 gram molecule or less per liter the equation gave good results. *C. L. S.*

Note on the Osmotic Theory of the Voltaic Cell. *H. M. Goodwin. Phys. Rev.* **4**, *242* *(1896)*. Experiments disproving the conclusions of the reviewer in respect to the anion. The point is well taken but has already been recognized. It is depressing to find the author stating that Paschen's measurements with mercury as electrode could have been predicted because there is a saturated solution formed while he ignores the measurements with zinc or cadmium as electrode where this explanation is untenable.

W. D. B.

On a Potential Regulator for Thermopiles. *H. Danneel. Zeit. Elektrochemie.* **3**, *81*, *(1896)*. In the Ostwald thermostat the supply of gas is diminished as soon as the temperature reaches a certain value. By means of a solenoid and a magnet a regulator has been constructed for the thermopile which checks the supply of gas whenever the potential difference between any two points in the circuit exceeds any desired value. This invention is of great importance for electrolytic analysis. *W. D. B.*

Iron Silicids. *G. de Chalmot. Zeit. Elektrochemie.* **3**, *85* (*1896*). To the hypothetical compounds Fe_2Si, FeSi, $FeSi_2$ is to be added Fe_3Si_2. The author's own experiments are fairly conclusive proof that these compounds do not all exist. *W. D. B.*

Apparatus for applying Richards's Process for the Separation of Gold and Silver by Volatilization. *W. Borchers. Zeit. Elektrochemie* **3**, *85* (*1896*). Richards volatilizes silver with the aid of a blast lamp. Borchers describes an apparatus for doing this in the electric furnace. *W. D. B.*

Conversion of Nitriles into Amins by Electrolysis. *F. B. Ahrens. Zeit. Elektrochemie.* **3**, *99* (*1896*). Nitriles are reduced to amins by the electrolysis of aqueous sulfuric acid or sodium hydroxid. The method is a thoroughly bad one because the nitriles are changed into acids by water. It is not stated whether any hydrogen escapes during the electrolysis. *W. D. B.*

On the Theory of the Lead Accumulator. *W. Löb. Zeit. Elektrochemie.* **3**, *100* (*1896*). Since lead superoxid is formed in a coherent mass at the anode and none is precipitated away from the electrodes, the author rejects the assumption of Elbs that lead superacetate is always formed as an intermediate product. While the conclusion may be sound, the reasoning is not. *W. D. B.*

The Electrolysis of Benzoic Acid. *W. Löb. Zeit. Elektrochemie,* **3**, *3* (*1896*). Sodium benzoate was electrolyzed at temperatures below 40° with a current of 30 amperes, the potential difference between the electrodes being 6 to 7 volts. The products of the electrolysis are carbon monoxid, carbon dioxid, hydrogen, oxygen, acetylene, benzaldehyde and a sodium salt which has not yet been identified. *W. D. B.*

On Electrochemical Units. *A. Wilke. Zeit. Elektrochemie,* **3**, *40* (*1896*). It is proposed to give a special name to the density of the current if a unit can be agreed upon which will satisfy both the scientific and the technical men. *W. D. B.*

INNER THERMODYNAMIC EQUILIBRIA

BY J. E. TREVOR

I. Introduction

The differential of the energy of any material system of given masses subject only to reversible actions of heating and compression is represented as

$$d\varepsilon = t d\eta - p dv \qquad (1)$$

where p and t denote the pressure and the (absolute) or thermodynamic temperature, η the entropy and v the volume of the total mass. For, the two terms of the second member of this equation represent the heat and work added to the system, and by hypothesis these are the work equivalents of the only actions exerted upon it from without. The energy of such a system is accordingly a function of its entropy and volume and is determined by these. This however is not in general true of a physically and chemically homogeneous phase of a material system, for the energy of a phase changes with the variation of the masses of its constituents. The state of a phase, and consequently the value of its energy, is wholly determinate when for given entropy and volume the masses of its constituents are given, so, as has been remarked by Gibbs[1], the energy of such a phase is a function of its entropy, its volume and the masses $m_1, m_2, \; . \; . \; . \; m_\nu$ of its several constituents, ν in number, and we can write

$$d\varepsilon' = t d\eta' - p dv' + \Sigma \mu dm' \qquad (2)$$

where for any constituent (i) the quantity μ_i is the mass derivative

$$\mu_i = \frac{\partial \varepsilon}{\partial m_i}$$

of the energy for this constituent (it is termed by Gibbs the potential of the latter) and the summation is extended over all the ν constituents. The constituents must be so chosen that the differen-

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[1] J. W. Gibbs. Trans. Conn. Acad. 3, 116 (1875).

tials of their masses are independent and can express every possible variation in the composition of the phase. The quantities $\varepsilon, \eta, v, m_1$, m_2, . . . m_ν in (2) have accents to indicate that they relate to a single phase and not to a system of phases, the accents are omitted from $t, p, \mu_1, \mu_2, \ldots \mu_\nu$ for the reason that these quantities have uniform values throughout all the coexistent phases of a system in equilibrium.[1]

In Gibbs's great paper on the equilibrium of heterogeneous substances it is shown that, although the form of the relation holding among the energy, entropy, volume and masses of a phase is not known, yet an integral expression involving these independent variables together with the energy and its partial derivatives can be obtained by integrating (2) for constant state—*i. e.*, for constant temperature, pressure and relative masses of the several constituents—from zero to a finite amount of phase. The operation is possible, because each potential, μ, is a function of the temperature, pressure and relative masses of the constituents,[2] and on increasing the masses at constant state all the quantities $\varepsilon, \eta, v, m_1, m_2, \ldots m_\nu$ increase in the same ratio. The result is a perfectly general expression

$$\varepsilon' = t\eta' - pv' + \Sigma\mu m' \tag{3}$$

for the energy of the phase,[3] whose differential must accordingly be

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[1] Gibbs. *l. c.* 119 and thereafter.

[2] Duhem. *Le Potentiel Thermodynamique*, 33 (1886).

[3] Gibbs *l. c.* 143. The form in which this operation is executed by Duhem is very interesting. Setting out from the idea of the thermodynamic potential for constant pressure, ζ, he says essentially that since an a-fold total mass of unvaried temperature, pressure and composition will have a-fold energy, entropy and volume, the function

$$\zeta = \varepsilon - t\eta + pv$$

is a homogeneous function of the first degree of the masses of the constituents [though it may indeed, and probably does, involve the ratios of these masses], and therefore from Euler's theorem of homogeneous functions

$$\zeta = \sum m \frac{\partial \zeta}{\partial m}$$

$$\varepsilon - t\eta + pv = \Sigma\mu m,$$

since for any constituent $\mu = \partial\zeta / \partial m$, as may readily be shown.

a general formulation of the differential of the energy, namely

$$\begin{aligned} d\epsilon' &= t d\eta' - p dv' + \Sigma \mu dm' \\ &+ \eta' dt - v' dp + \Sigma m' d\mu. \end{aligned} \qquad (4)$$

But equation (2) is also general, so there follows from (2) and (4)

$$o = \eta' dt - v' dp + \Sigma m' d\mu, \qquad (5)$$

a general relation for all reversible changes of state of the phase.[1] From this remarkable equation Gibbs had deduced very important results,—the magnificently simple and comprehensive Phase Rule for one thing,[2] and a series of theorems relating to the vapor pressure curves of liquid mixtures,[3] to cite no further examples.

Now this deduction of Gibbs, as it stands, is just in so far unsatisfactory as the terms of equation (5) lack interpretation ; its *correctness* indeed is obvious, but its *meaning* is not. We may have fairly clear ideas of the energy, entropy, volume, temperature and pressure of a phase, of the masses and potentials of its constituents, of the differential of its energy and of the quantities

$$t d\eta' \qquad p dv' \qquad \mu_i dm_i'$$

of heat, work and chemical energy added reversibly to it,—but what does $\eta' dt$ denote, or $-v' dp$ or $\Sigma m' d\mu$, and what is the signification of their algebraic sum appearing in equation (5) ? What also is the signification to be attached to the various terms of the second member of (3) ? To seek the interpretation given by the energy theory to these different quantities is the object of the present paper ; the results of the investigation should add meaning to the equation (5) and thus make the deductions from it seem more reasonable and therefore more intelligible and satisfactory.

II. Individual Phases

A part of the problem has been worked out by Helmholtz in his development of the theory of free energy, where for any thermodynamic system suffering reversible change the quantity ηdt is looked upon as « the amount of free energy transformed into bound [energy]

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[1] Gibbs. *l. c.* 143.

[2] Ibid. *l.c.* 152.

[3] Ibid. *l. c.* 155.

during every rise of temperature in the system »,[1] but this tells us nothing about vdp so it is evident that the whole question must be examined in a somewhat more general way. Let us attend more closely to equation (4)

$$\begin{aligned} d\epsilon' &= td\eta' - pdv' + \Sigma\mu dm' \\ &+ \eta' dt - v' dp + \Sigma m' d\mu. \end{aligned} \qquad [4]$$

It represents the complete differential of the energy of the phase, relating both to the accession of energy from without in any change and to all possible concomitant changes of energy within the phase. We know the accessions from without to be represented by the first $\nu + 2$ terms of the second member, namely by the first row in the equation as written, and since the total amount of the energy can change only through (positive or negative) accessions from without it follows that the inner rearrangement of the parts of the energy, as these are consequent upon any reversible disturbance of the state of the phase, are represented by the second row of this member and must exactly compensate one another—we must have the Gibbs equation

$$o = \eta' dt - v' dp + \Sigma m' d\mu\,;$$

the terms of this equation are all energy terms of course. Inner heatings (positive or negative), inner compressions and inner variations in the chemical energies of constituents may result from changes which the phase is made to undergo, but when these changes are measured by their work equivalents—in energy terms namely—they must balance one another.

The particular signification of the terms in question is obtained perhaps better if the differentiation examined, that of equation (3), be written out in full. We have for the phase in any fixed state

$$\epsilon' = t\eta' - pv' + \Sigma\mu m' \qquad [3]$$

which differentiates to

$$d\epsilon' = \begin{cases} d(t\eta') = td\eta' + \eta' dt \\ d(-pv') = -pdv' - v' dp \\ d\Sigma\mu m' = \Sigma\mu dm' + \Sigma m' d\mu \end{cases} \qquad (5)$$

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[1] Helmholtz. Sitzungsber. Akad. Wiss. Berlin **1882.** Also Wiss. Abh. **2,** 976. Also the very excellent and convenient translation of five of Helmholtz's electrochemical papers, published by the Physical Society of London, page 60.

and here it must be noted that the differential of the energy, the sum of the work equivalents of all outer actions, appears as the first column of the right hand member, while the accompanying inner rearrangements of the energy of the phase—which necessarily sum up to zero—appear in the second column. The signification, now, of the integral expressions

$$t\eta' \qquad -pv' \qquad \Sigma\mu m'$$

appears at once from their differentiation. The first of them, $t\eta'$, changes uniformly with incoming or outgoing heat, $td\eta'$, and may therefore be looked upon as that portion of the total energy of the phase which is potential with respect to heat,—it may be termed the *heat function*. The second, $-pv'$, changes uniformly with work, $-pdv'$, taken up or developed, it is a function which is potential with respect to work,—it is the *work function*. The third, $\Sigma\mu m'$ or $\epsilon' - t\eta' + pv'$, the ‹thermodynamic potential› ζ', of these integral quantities is that portion of the energy which changes uniformly with the production or absorption of chemical work, $\Sigma\mu dm'$,— it might be termed, for the simple conditions here considered, the *chemical function* of the phase. Nothing, now, that

$$\Sigma m'd\mu = -\eta'dt + v'dp$$

we read from equation (5) that, in any reversible change of state of a phase: All heat is developed at the expense of the heat function, and this latter is transformed into the work and chemical functions by the amount $-\eta'dt$ if the temperature rise; all work is produced at the expense of the work function, which is transformed into the heat and chemical functions by the amount $v'dp$ if the pressure rise; and all chemical work appears at the expense of the chemical function ζ', which is at the same time transformed into the heat and work functions by the amount

$$\eta'dt - v'dp = -\Sigma m'd\mu$$

through any variation in the temperature or the pressure. It should be noticed that variations in the relative masses (concentrations) of constituents do not cause variation in the value of the chemical function $\Sigma\mu m'$ although they change the values of certain of the potentials; such variations merely effect redistribution among the terms of the sum

$$\mu_1 m_1 + \mu_2 m_2 + \ldots\ldots + \mu_n m_n$$

without altering its total value. The simplification of statement which results from the introduction of conditions of constant temperature or pressure during change are too apparent to call for separate comment.

The foregoing considerations suffice to give an obvious energy interpretation to the quantities

$$t\eta' \qquad -pv' \qquad \Sigma\mu m'$$

and to the terms

$$\eta' dt \qquad -v'dp \qquad \Sigma m' d\mu,$$

the former are functions potential with respect to the different kinds of action of which the phase is capable, while the latter are the quantities of energy which are transformed from one of these functions to others through concomitant changes in the temperature or pressure. When the total energy of the phase is resolved into pairs of functions, through successive combination of the three just discussed, and these pairs are represented for brevity by the symbols

$$\psi' = -pv' + \Sigma\mu m' = \varepsilon' - t\eta' \qquad (6a)$$

$$\chi' = t\eta' + \Sigma\mu m' = \varepsilon' + pv' \qquad (6b)$$

$$\varphi' = t\eta' - pv' = \varepsilon' - \Sigma\mu m', \qquad (6c)$$

the equation (5) for the differential of the energy takes the following forms :

$$d\varepsilon' = \left\{ \begin{array}{rll} d(t\eta') = & td\eta' & + \eta' dt \\ d\psi' = & -pdv' & \\ & + \Sigma\mu dm' & - \eta' dt \end{array} \right. \qquad (7a)$$

$$d\varepsilon' = \left\{ \begin{array}{rll} d(-pv') = & -pdv' & - v'dp \\ d\chi' = & td\eta' & \\ & + \Sigma\mu dm' & + v'dp \end{array} \right. \qquad (7b)$$

$$d\varepsilon' = \left\{ \begin{array}{rll} d\,\Sigma\mu m' = & \Sigma\mu dm' & + \Sigma m' d\mu \\ d\varphi' = & td\eta' & \\ & -pdv' & - \Sigma m' d\mu. \end{array} \right. \qquad (7c)$$

In thermodynamic changes, as described for example, by (7*a*) all work and chemical energy furnished by the phase are supplied at the expense of the function ψ' and all heat at the expense of $t\eta'$, while, if the temperature change, ψ' is transformed into $t\eta'$ by the amount $\eta' dt$.[1] Similar interpretations may be given to the forms (7*b*) and (7*c*).

III. ‹*Open Systems*› *of Phases*

If we consider as our thermodynamic body a system of coexistent phases, instead of a single phase, we shall form an expression for the total energy of the system by summation, over all the different phases, of the equation (3)

$$\varepsilon' = t\eta' - pv' + \Sigma \mu m'$$

for the energy of each one. The masses making up the whole are still supposed to be independently variable,—the body is not a ‹closed› system, it is an *open* one. The summation gives

$$\varepsilon = t\eta - pv + \Sigma \mu m, \qquad (8)$$

where the unaccented letters refer to the entire mass; for, the temperature, pressure and potentials have uniform values throughout, and the energy, entropy, volume and masses are additive. The differential of the energy is found by a similar summation of

$$d\varepsilon' = td\eta' - pdv' + \Sigma \mu dm'$$

as

$$d\varepsilon = td\eta - pdv + \Sigma \mu dm, \qquad (9)$$

as is indeed obvious anyway since the energy of a heterogeneous system of varying masses subject only to actions of heating and compression is determined by the values of its entropy, its volume and the masses of its constituents—the constituents being as before so chosen that the values of the different *dm*s are independent. A general expression for the differential of the energy is likewise to be obtained by differentiation of (8), which gives

$$\begin{aligned} d\varepsilon = {} & td\eta - pdv + \Sigma \mu dm \\ & + \eta dt - vdp + \Sigma m d\mu \end{aligned} \qquad (10)$$

or, because of (9),

$$0 = \eta dt - vdp + \Sigma m d\mu \qquad (11)$$

for the entire system. The interpretation of these equations must remain the same as in the more special case of a single phase,—the

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[1] Compare Helmholtz, as previously cited, page 60.

equation (10) represents the total differential of the energy in all its changes both within and without the system, equation (9) asserts this differential to be the sum of the work equivalents of all outer actions added, whence follows (11) that the inner redistributions of parts of the energy, as consequent upon any reversible disturbance of the state of the system, must compensate one another to maintain the inner equilibrium.

The entire matter may, accordingly, as before be represented in a single expression by writing

$$d\varepsilon = \left\{ \begin{array}{rcll} d(t\eta) & = & t d\eta & + \eta dt \\ d(-pv) & = & -pdv & - vdp \\ d\Sigma \mu m & = & \Sigma \mu dm & + \Sigma m d\mu, \end{array} \right. \qquad (12)$$

where the two vertical columns of the right hand member represent respectively the accessions of energy and the innner rearrangements consequent upon change—the total value of the second column always disappearing. It is seen from the differentiation (12) that the *heat function*, $t\eta$, of the system is that portion of the total energy which is potential with respect to reversible heat; the *work function*, $-pv$, is potential with respect to reversible compression-work; while the remainder of the energy, the quantity $\varepsilon - t\eta + pv$ or $\Sigma \mu m$, the *chemical function* in this particular case, the thermodynamic potential $\zeta = \varepsilon - t\eta + pv$ in general, is transformed into the other two in proportion as the temperature and the pressure suffer change. In any reversible thermodynamic variation of state there occurs a redistribution among these potential functions, such that ηdt is transferred to the heat function if the temperature change and $-vdp$ to the work function if the pressure change, the algebraic sum of both, $-\Sigma m d\mu$, being contributed by the chemical function to maintain the inner equilibrium.

It may be noted in particular that in a compression the energy $-pdv$ is added to the work function, but the quantity vdp is transferred therefrom to the heat and chemical functions if the pressure rise,—the energy added does not in general increase the work function *alone*. Similarly, on heating, the energy $td\eta$ is added to the heat function, but at the same time the quantity ηdt is contributed thereto by the other functions to restore the inner equilibrium if the temperature rise, but is gained by them if it fall,—the added energy again not coming solely to the good of the function through which the supply of energy to the system is introduced. This is somewhat as though work were added to a strained spring fastened to the piston confining an air cushion in a cylinder; the energy added is not stored wholly in the increased potential energy of the spring, it is transferred in part, through compression, to that of the air cushion—to restore the inner equilibrium of the system.

It may be said in general that all addition of heat increases the heat function and all addition of work the work function, while through change of temperature the energy ηdt is transferred from the chemical function to the heat function and through change of pressure the energy vdp passes from the work function to the chemical one—to the thermodynamic potential ζ.

These general relations assume what may possibly be considered a somewhat simpler form when the above potential functions are combined into pairs, as was done in studying the behavior of single phases. We will put

$$\psi = -pv + \Sigma\mu m = \varepsilon - t\eta \qquad (13a)$$
$$\chi = t\eta + \Sigma\mu m = \varepsilon + pv \qquad (13b)$$
$$\varphi = t\eta - pv = \varepsilon - \Sigma\mu m \qquad (13c)$$

and consequently

$$d\varepsilon = \left\{ \begin{array}{rl} d(t\eta) = & td\eta \quad + \eta dt \\ d\psi = & -pdv \\ & \quad + \Sigma\mu dm - \eta dt \end{array} \right. \qquad (14a)$$

$$d\varepsilon = \left\{ \begin{array}{rl} d(-pv) = & -pdv \quad - vdp \\ d\chi = & td\eta \\ & \quad + \Sigma\mu dm + vdp \end{array} \right. \qquad (14b)$$

while the form with φ is best left in the shape (12) where $d(t\eta)$ and $d(-pv)$ can readily be considered together.

Helmholtz has termed the work and heat functions of (14*a*) the «free» and «bound» energies of the system for isothermal changes, the former being free for conversion into work while the latter is bound in this respect; the former, namely, is the potential energy with respect to work, the latter is potential with respect to heat only.

This terminology can be applied to both (*14a*) and (*14b*). The former asserts that in isothermal changes all work is produced at the expense of the free energy and all heat at the expense of the bound, while free energy is transformed into bound by the amount ηdt if the temperature rise. This was clearly recognized by Helmholtz[1] and it supplies in so far the interpretation to be given to the quantities ηdt and $t\eta$, as was stated by him in his famous first paper on the free energy theory. Equation (*14b*) asserts on the other hand that in isobaric changes work is produced at the expense of the free energy, $-pv$, and heat at the expense of the bound,[2] χ, while free energy is transformed into bound by the amount vdp if the pressure rise. This latter conception is, to be sure, in so far more artificial than the former as neither $-pv$ nor $\varepsilon + pv = \chi$ can be considered as positive parts of the total energy of the system, and, too, the «bound» energy is not bound in this case as regards the production of *chemical* work; its usefulness nevertheless is no wise impaired by these considerations. The third form of statement, that with φ, reads that all external actions are produced at the expense of the *action function* φ, while the latter is transformed into the chemical function $\Sigma\mu m$ (the energy of the «air cushion») by the amount

$$\Sigma m d\mu = -\eta dt + vdp$$

through such concomitant variations of temperature or of pressure as may arise.

IV. Closed Systems of Phases

For closed systems of phases, *i. e.* homogeneous or heterogeneous systems of fixed quantities of substances, the whole matter is simplified by the disappearance of all quantities of chemical work done upon the system or by it. The energy of the entire mass becomes a function of its total entropy and volume simply and we have, as at first,

$$d\varepsilon = td\eta - pdv.$$

The total differential (10) of the energy may then be written

$$d\varepsilon = td\eta - pdv$$
$$+ \Sigma\mu dm + \eta dt - vdp + \Sigma m d\mu$$

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[1] Helmholtz. l. c. page 60 of the Physical Society's translation.

[2] Compare Gibbs, l. c. 148.

whence

$$0 = \eta dt - vdp + \Sigma\mu dm + \Sigma m d\mu$$

$$d\Sigma\mu m = -\eta dt + vdp \qquad (15)$$

so that

$$d\varepsilon = \begin{cases} d(t\eta) = td\eta + \eta dt \\ d(-pv) = -pdv - vdp \\ d\Sigma\mu m = -\eta dt + vdp. \end{cases} \qquad (16a)$$

The state of affairs is here simply that in any reversible change, all heat is produced from the heat function and all work from the work function, while the chemical function gains $-\eta dt$ and vdp from the former and the latter through any changes of temperature or pressure which occur; the simile of the air cushion applies with peculiar force to the behavior of the chemical function ζ in this case. In the more special modes of description employing the functions ψ or χ we write

$$d\varepsilon = \begin{cases} d(t\eta) = td\eta + \eta dt \\ d\psi = -pdv - \eta dt \end{cases} \qquad (16b)$$

$$d\varepsilon = \begin{cases} d(-pv) = -pdv - vdp \\ d\chi = td\eta + vdp \end{cases} \qquad (16c)$$

which assert simply that, whether the free and bound energies for isothermal or for isobaric changes be considered, all work done, $-pdv$, is produced from the free energy and all heat, $td\eta$, from the bound, while in the former case ηdt is the energy transferred from the free energy to the bound if the temperature change, and in the latter vdp is that passing from the free to the bound through changes of pressure.

V. The General Case

There remains now merely to extend these considerations to the generalized case in which the working system can produce reversible actions other than effects of heating, compression and the transfer of masses, as for example in the production of an electric current. In such a case the state of the system requires for its determination a number of parameters c_1, c_2, . . . in addition to the entropy, volume and masses previously considered, and we must write

$$d\varepsilon = t d\eta - p dv + \Sigma \mu dm + \Sigma C dc \qquad (17)$$

where C_j is set for the derivative $\partial\varepsilon/\partial c_j$ and the second summation extends over all the new parameters. If we differentiate the quantity

$$\zeta = \varepsilon - t\eta + pv,$$

termed ζ consistently by Gibbs but written often as $\Sigma\mu m$ in the foregoing special cases, we shall have

$$d\zeta = d\varepsilon - t d\eta + p dv - \eta dt + v dp$$

and, on comparison with (17),

$$d\zeta = \Sigma \mu dm + \Sigma C dc - \eta dt + v dp. \qquad (18)$$

We can now write

$$\left\{\begin{array}{rll} d(t\eta) = & t d\eta & + \eta dt \\ d(-pv) = & - p dv & - v dp \\ d\zeta = & \Sigma \mu dm & - \eta dt \\ & + \Sigma C dc & + v dp \end{array}\right. \qquad (19a)$$

which is seen again to be the total differential of the energy of the system. For the first column of the second member is this differential, by (17), and the second is zero. So the interpretation of the quantities

$$t\eta \qquad -pv \qquad \zeta \qquad -\eta dt \qquad v dp$$

remains in this general case much as in the simpler ones previously studied: All work is supplied by the work function and all heat by the heat function, while through any changes of temperature or pressure which arise there result transfers of $-\eta dt$ and $+v dp$ from the heat and work functions respectively to ζ — the «thermodynamic potential for constant pressure» of Duhem, the characteristic function $-H'$ of Massieu. The thermodynamic potential takes charge of the inner equilibrium of the system.

With use of the potential functions

$$\psi = \varepsilon - t\eta$$
$$\chi = \varepsilon + pv$$

the equation (19a) assumes the forms

$$d\varepsilon = \left\{\begin{array}{rll} d(t\eta) = & t d\eta & + \eta dt \\ d\psi = & - p dv & \\ & + \Sigma \mu dm & \\ & + \Sigma C dc & - \eta dt \end{array}\right. \qquad (19b)$$

$$d\varepsilon = \left\{ \begin{array}{ll} d(-pv) & = -pdv - vdp \\ d\chi & = td\eta \\ & \quad + \Sigma\mu dm \\ & \quad + \Sigma Cdc + vdp. \end{array} \right. \qquad (19c)$$

From these it appears that, even in this general case, all heat is produced from the bound energy, $t\eta$, and all outer work

$$\textit{outer work} = -pdv + \Sigma\mu dm + \Sigma Cdc$$

from the free energy, ψ, while free energy is transformed into bound by the amount ηdt if the temperature change;[1] that, further, all heat and non-mechanical forms of work are produced from the bound energy, χ, and all mechanical work from the free, $-pv$, while through changes of pressure the latter is converted into the former by the amount vdp.[2]

So, in every possible case: 1. The function

$$\chi = \varepsilon + pv$$

is potential with respect to all possible isobaric action save compression work, and it changes by vdp if the pressure change; 2. The function

$$\psi = \varepsilon - t\eta$$

is potential with respect to all possible isothermal work (wholly convertible work equivalents), and it changes by $-\eta dt$ if the temperature change; and 3. The function

$$\zeta = \varepsilon - t\eta + pv$$

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[1] Compare Helmholtz, *l. c.*

[2] Helmholtz (*l. c.* 59) has termed the entropy "The heat-capacity for heat produced at the expense of the free energy ψ during adiabatic change". This is indicated directly by (19*b*), in particular by the formulation

$$-\frac{\partial\psi}{\partial t}\,dt = \eta dt = \frac{\partial(t\eta)}{\partial t}\,dt.$$

The analogous remark derived from (19*c*) and relating to the volume is that—The volume is the work capacity for compression produced at the expense of the free energy, $-pv$, in adiabatic changes when all work done is compression work. For we note that

$$-\frac{\partial(-pv)}{\partial p}\,dp = vdp = \frac{\partial\chi}{\partial p}\,dp.$$

is potential for all actions save heating and the production of compression work, and it changes with temperature and pressure by the amount

$$-\eta dt + vdp.$$

It may be said, finally, that the energy quantity

$$\eta dt$$

is in every case transferred through change of temperature from the integral function which is potential with respect to non-mechanical forms of work, to that which is potential for heat; and that the energy

$$vdp$$

is always transferred through change of pressure from the function which is potential with respect to mechanical work to that potential with respect to non-mechanical work[1] (not heat). The former represents the heat produced in the system from its stock of wholly convertible work equivalents and the latter represents compression stored there at the expense of the system's capacity for producing mechanical work. The generality of these relations is perhaps easier seen when the equations (19*a*) to (19*c*) are written out more in full—as follows:

$$d\varepsilon = \begin{cases} d(t\eta) = & td\eta & + \eta dt \\ d(-pv) = & -pdv & - vdp \\ d\zeta = & \Sigma\mu dm & - \eta dt \\ & + \Sigma C dc & + vdp \end{cases} \qquad (19a)$$

$$d\varepsilon = \begin{cases} d(t\eta) = & td\eta & + \eta dt \\ d\psi = & -pdv & - vdp \\ & + \Sigma\mu dm & - \eta dt \\ & + \Sigma C dc & + vdp \end{cases} \qquad (19b)$$

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[1] My attention has been caught by a footnote in a paper by L. Natanson, *Zeit. phys. Chem.* **10**, 741, (1892), where the quantities ηdt and vdp are termed the *transformed heat* and the *transformed work* of the system. The source cited is Natanson's *Theoretische Physik*, which however has appeared only in Polish and is not accessible to me. It seems probable that this author had in mind some such view as the above. Later: See, however, the note at the close of this article.

$$d\varepsilon = \left\{\begin{array}{rlll} d(-pv) = & -pdv & & -vdp \\ d\chi = & tdη & & +ηdt \\ & +\Sigma\mu dm & & -ηdt \\ & +\Sigma Cdc & & +vdp \end{array}\right. \qquad (19c)$$

the statements made are verified in each of the three.

The first (19*a*) of these equations has for simplicity of statement and readiness of interpretation much to recommend it, and this may account in some measure for the prominent part taken in recent years by the thermodynamic potential ζ in the development of the theory of chemical equilibria; the appearance here, too, of the temperature and pressure as independent variables is an advantage not offered by the other forms of statement. The important equations of the potential theory, when it is cast into this form, are then (for the case where the differentials dc disappear)

$$\begin{aligned} d\zeta &= \Sigma\mu dm - \eta dt + vdp \\ 0 &= \eta dt - vdp + \Sigma m d\mu, \end{aligned}$$

their interpretation is greatly aided by the foregoing considerations.

The view advocated in the present paper is, briefly, that just as

$$d\varepsilon = td\eta - pdv + \Sigma\mu dm$$

represents the change of the energy of a material system, as dependent directly upon actions from without, so is the sum

$$\eta dt - vdp + \Sigma m d\mu = 0$$

to be regarded as denoting the mutually compensating changes of the energy, which arise within the system itself when actions occur. The individual terms of this sum may then be regarded very suitably as the quantities of energy which are transformed from certain of the potential functions of the system into others during change of temperature or pressure—the potential functions themselves maintaining their general significations thereby.[1]

Cornell University, December 1896.

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[1] After this paper was in type the writer discovered very unexpectedly that the general features of the view which it presents are contained in a brief

article by L. Natanson in *Wiedemann's Annalen*, **42**, *178* (*1891*), which had been altogether overlooked. It has seemed best all the same, upon due consideration, to allow the paper to appear, and this for the reasons that the more detailed discussion here given may have some value in aiding a comprehension of the matter, that the present statement bears immediately upon certain general formulas of great importance in Gibbs's theory of thermodynamic equilibria—especially upon the interpretation to be given to his very remarkable equation (97), and also because the view in question does not seem to have received the recognition which it deserves—as is evinced by the absence of any employment of it in the text books of van Laar (1893) and of Helm (1894) on the thermodynamics of chemical processes.

AN EXAMINATION OF THE ABEGG METHOD OF MEASURING FREEZING-POINT DEPRESSIONS

BY E. H. LOOMIS

Under the title, «Depression of the Freezing Point in very Dilute Solutions,»[1] Abegg has recently described various modifications of his former method[2] which have greatly increased its accuracy. Besides repeating the measurements made with the earlier method on NaCl, cane sugar and alcohol, he has determined, in addition, the freezing points of the following solutions:—KCl, K_2SO_4, tartaric acid, grape sugar and urea. It is to be regretted that he did not subject $MgSO_4$ and KNO_3 to the same careful examination, since it will be remembered that these salts according to the measurements of Loomis exhibit a marked departure from the theory which Arrhenius proposed and which Abegg accepts. The mere fact that NaCl, KCl, K_2SO_4 and the great majority of the compounds examined by me seem to support this theory strongly, makes it, I think, the more important that those, at least, who accept the theory, should in their work of repeating the investigations of other observers, give careful attention to the solutions which present exceptions. Any broadening of the present theories must come by a critical examination of the exceptional cases, and these need first of all to be established upon a sure experimental basis before any modification or extension of present theories may be safely undertaken. In regard to all hasty efforts in this direction the words of caution which Abegg himself expresses (page 232) are most timely:—«Neither the extent nor certainty of the present experimental data is sufficient to furnish a sure foundation for speculation.» These words, specifically uttered with sole reference to his own work, the great accuracy of

[1] Abegg. Zeit. phys. Chem. **20**, 207 (1896).
[2] Nernst and Abegg. Ibid. **15**, 681 (1894).

which appears to the most hasty as well as to the most critical reader, could, I think, be wisely appropriated by all workers in this field of research.

The present work commends itself for the manifest purpose of the observer to secure exact results whatever may be their bearing on any accepted theory ; and it is hoped for this reason that the work will be extended over a large range of characteristic compounds. The great need at present is a broader basis of well established experimental facts.

In regard to the present method of Abegg, one observes that it differs from the earlier method (Nernst and Abegg) in the following particulars :—

1. The substitution of a mixture of salt water and fine ice in place of the former «cryohydrate» in the production of the cold bath of constant temperature outside the air mantle in which the «freezing vessel» is placed. This cold bath is kept at a constant temperature a few tenths of a degree below 0°C. (Loomis)

2. The substitution of an automatically regulated mechanical stirrer for the former hand stirrer. (Abegg)

3. The increase of the dimensions of the apparatus so that 1000 *cc.* of the solution are used instead 100 *cc.* (Jones)

4. The use of a mechanical vibrator for jarring the thermometer while in use. (Pickering[1])

5. The initial overcooling, which the solutions undergo before freezing begins, was not allowed to exceed 0.8°C, in general it was 0.5°C. (L.) In the former method this overcooling was left to take care of itself and usually reached 1.30°C.

These modifications in the method together with the fact that the work is now done at a room-temperature usually below 6°C enable Abegg to dispense with the corrections which had to be applied to the results obtained with the earlier method as follows :—

First, the adoption of the ice and salt water mantle, the temperature of which is kept a few tenths of a degree below 0°C (L.),

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[1] This jarring of all finely divided thermometers, now generally known to be indispensable to their accurate performance, while universally credited to Loomis, was introduced by S. U. Pickering in his calorimetric work in 1886. See Phil. Mag. (5) **21**, 330 (1886) and Jour. Chem. Soc. **51**, 294 (1887).

together with the fact that the room temperature was lowered to a point as near 0°C as the method would permit (L.) has brought the «convergence temperature» to such close coincidence with the true freezing point of the solution that the correction for the different values of the Nernst and Abegg constant K in different solutions vanishes.

Second, the restriction of the overcooling of the solution to the small average amount of 0.5°C makes it no longer necessary to apply the correction for changes in the concentration of the solution due to the separation from the solution of a considerable part of the solvent in the form of «ice».

The former correction was first theoretically calculated by Nernst and Abegg, as well as experimentally verified by them, and is undoubtedly valid.

The latter correction has only a rough theoretical foundation and, so far as is known to me, has had no experimental verification. It was undoubtedly Abegg's effort to eliminate this uncertain correction that led to the modifications of his former method. These modifications at the same time necessarily eliminated the other correction, since any attempt to confine the overcooling to a small amount, with the purpose of having a very small quantity of ice present in the solution, at once requires that the solution be completely isolated from the disturbing outside temperatures. *This was the fundamental idea in the Loomis method* (1893). It may not be out of place here to refer to the original publication of this method in Wiedemann's Annalen, **51**, 504 (1894) where the following words are found: «*Es liegt somit die Nothwendigkeit vor die Flüssigkeit deren Gefrierpunkt bestimmt werden soll, vor den störenden Einflüssen der Aussentemperaturen zu schützen.*» Accordingly the overcooling was confined to the limits 0.15°C—0.25°C and the freezing vessel was surrounded with an air bath protected, *except at the top*, with an auxiliary cold bath of constant temperature 0.3°C below that of the freezing point of the solution. To guard against the disturbing influence of the air, the freezing tube was made very long and the solution was confined to its lower extremity, so that it was deeply submerged in the «protection bath». To provide still farther against any disturbance due to the room-temperature, the room-temperature was lowered until it was as near 0°C as the season of the year would permit. All subsequent measurements have been made at about 3°C. I have taken several occasions to emphasize my belief that a last degree of exactness in freezing point work is to be looked for only when the room temperature is kept constant at 0°C. This has thus far been impossible with the facilities which have been at my command. That these experimental precautions, developed after many thousand observations of the freezing-point of pure water, resulted in the complete elimination or perhaps better *balancing* of all the disturbing influences, was established, I think, by the long series of experiments which showed that the thermometer gave sensibly the same readings when only mere *traces* of ice were present as when there were large quantities in the water[1]. It seems fair to assume that this would have been impossible if the «convergence temperature» had not been practically identical with the *true* freezing point of the solution, and my original conclusion seems to be abundantly justified, namely, that «The disturbing influences of the freezing bath and the air were so far eliminated that the *actual* freezing point of water as well as that of a dilute solution may be determined with the greatest certainty.»[2] The word «actual» was here employed to distinguish the true freezing point from what Nernst and Abegg call the «apparent» freezing point. This reference is sufficient explanation of the fact that I have never thought it necessary to examine my method «with reference to the sources of error which Nernst and Abegg discovered» and will leave, I think, little reason for them «to wonder».

It may be safely accepted that the convergence temperature plays no rôle in the results obtained by the Loomis method. The almost complete identity of these later results of Abegg (1896) with those obtained by me (1893) is additional ground for believing that this conclusion is valid. See for example Fig. 8, where the results of these observers for alcohol are graphically represented. While it thus appears that, in main features, the present method of Abegg is essentially that introduced by Loomis, it must not be overlooked that Abegg has very ingeniously protected his freezing vessel

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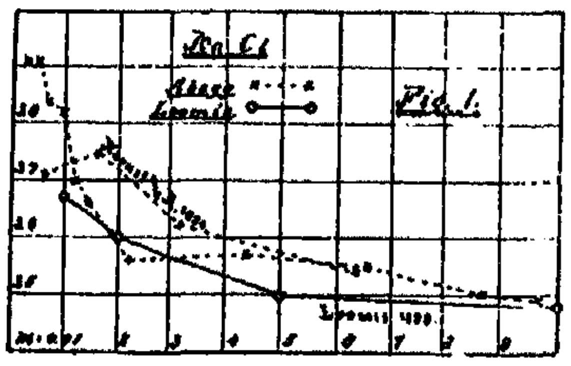
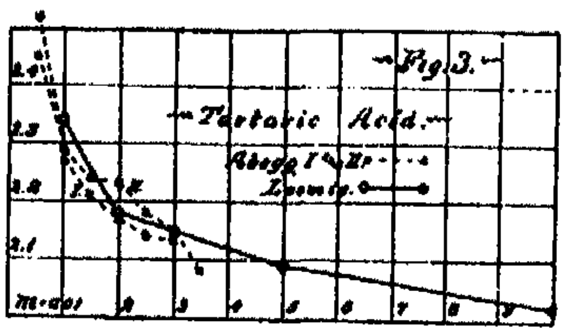
[1] Wied. Ann. **51**, 511 (1894).

[2] See Phys. Rev. **1**, 213 (1893).

above so that there is the most complete isolation of his solutions from the room temperature and he is thus able to secure good results even at ordinary room temperatures. He has also introduced successfully a mechanical stirrer, and thus justly claims to have barred out the last possibility of the observer's bias affecting the results. This is an advance by no means insignificant. In connection with my work I have found, however, after proper precautions are taken to eliminate the observer's bias, and when his only concern is to stir the solution uniformly, that hand stirring is entirely permissible and is so sensibly uniform that no appreciable errors are introduced from this cause. In regard to the value of increasing the quantity of the solution as Abegg has done, in accordance with the suggestion of Jones, from 100 *cc.* to 1000 *cc.*, I think there is some doubt. Following the same suggestion I increased the quantity from 70 *cc.* to 250 *cc.* but failed to observe any reduction in the experimental errors. Abegg does not call attention to any facts that would lead us to believe that this change has contributed anything to the accuracy of his new method.

We are now ready to pass to an examination of the new results themselves. Without giving the data in tabular form they are graphically represented Figs. 1–8, where the x———x———x lines represent Abegg's values of the molecular depression. Ordinates are molecular depressions and abscissæ are gram-molecular strength of the solutions (gram. mol. per liter of the solution). The o———o———o lines in the figures are the corresponding values found by Loomis.



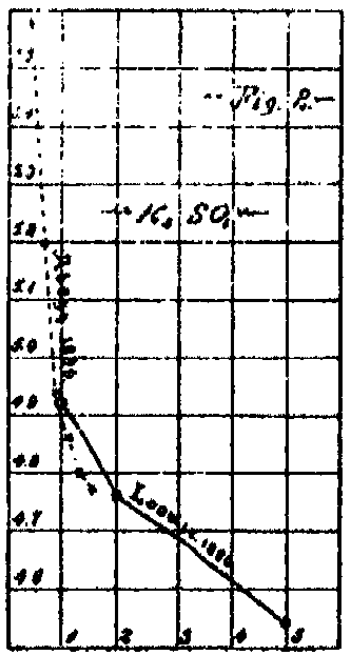


1. By an examination of these «curves» it appears, that, barring zigzags, they present in general a most gratifying agreement with those obtained by me. This agreement is so close in all cases except cane sugar and urea in extreme dilution ($m = 0.01 - 0.02$)

as to amount to little less than an identity. Thus, taking the measurements for the 1/100 normal solutions and «smoothing» out the various curves as far as experimental errors will justify we find the following differences between the measurements of Abegg and Loomis :—

NaCl	+0.0010°	Cane Sugar	+0.0016°
K_2SO_4	0.0000°	Grape Sugar[1]	—0.0007°(?)
Tartaric Acid[1]	—0.0005°	Urea	+0.0013°
KCl	+0.0003°	Alcohol	+0.0006°

These differences can hardly be looked upon as large even in the extreme cases of cane sugar and urea ; and they practically disappear altogether in the regions of greater concentration. It is not to be overlooked that these differences between Abegg's results and those found by me are *less* than the differences exhibited by the two parallel series of observations made by Abegg himself on the respective solutions. For a tabular exhibit of these differences the reader is referred to Abegg's paper.[2] The full significance of these facts appears very strongly in the results for tartaric acid, KCl, and alcohol. (See Figs. 2, 4, 8.) I may be allowed the privilege of expressing here my deep satisfaction at this splendid verification of my early work by such careful and conscientious investigators as Nernst and Abegg, especially in the case of the alcohol results, which have so long stood alone, and which the former work of Nernst and Abegg certainly did not confirm. That the greater accuracy of Abegg's new method should result in such close duplication of my values is most gratifying. I am however unable to agree with Abegg in his explanation of the *low* values for alcohol, namely, that they arise



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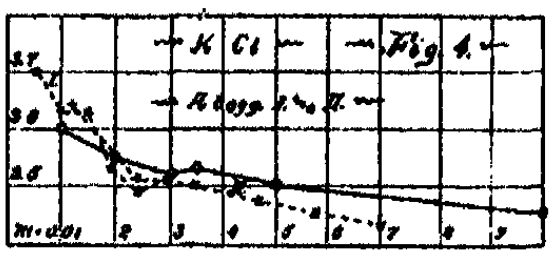
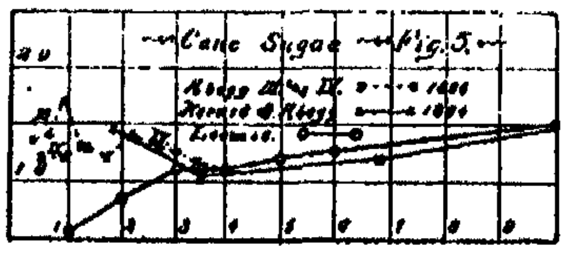
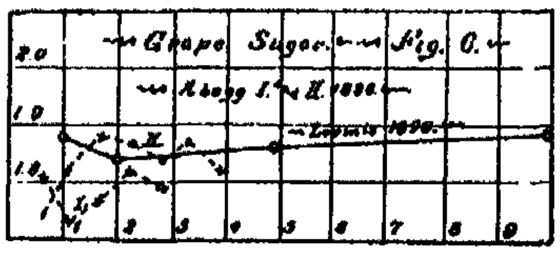
[1] Princeton Bulletin, **1896**, Oct. page 56.

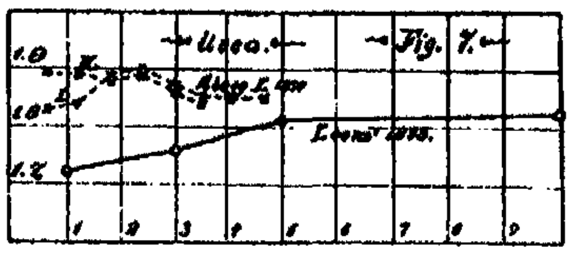
[2] Zeit. phys. Chem. **20**, 224 (1896).

from inaccuracies in the generally accepted specific gravity tables,[1] particularly since such explanation would require that these tables are about five per cent wrong. I am not aware that the extensive and widely varied work on the properties of alcohol solutions has ever before raised any such suspicion. Quite recently Wildermann has similarly sought to explain the low values which I found for urea by supposing that I incorrectly determined the strength of the original solution. Such an explanation is not at all improbable, and makes it desirable that the observers who repeat this work should start out from a normal solution of the compound prepared by direct weighing, and that they should then carefully determine its specific gravity after making sure that the urea is pure. The urea which I employed was the ordinary *c. p.* compound prepared by Henn and Kittler, Strasburg, and was used without recrystallization. The sp. gr. $\left(\frac{18^\circ}{4^\circ}\right)$ of the «normal» solution (normal at 6°C) was 1.0148. These data would enable any chemist to decide how much in error my «normal» solution must have been.









2. An examination of the experimental results affords the means for a trustworthy estimation of the method's accuracy.

It is to be observed in the first place that the careful isolation of the solution from disturbing influences together with the great uniformity of the stirring and extremely constant temperature of the

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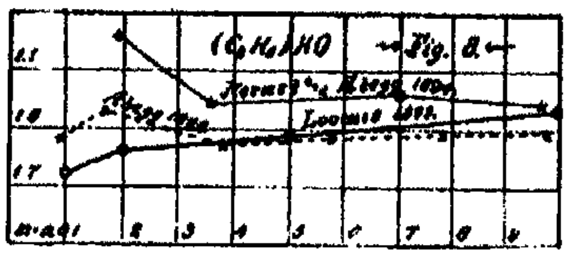
[1] Those of Mendelejeff were used in my work on alcohol. Abegg does not indicate whose tables he employed.

«protection bath» enable Abegg to attain an absolutely stationary mercury column, which according to his direct experiments could be maintained continuously for *three hours*, during which time no variation amounting to 1/10000 of a degree was observed.

May it not be asked if this surprising constancy may not be misleading? It certainly has proved so in the 1/100° thermometer used by me, and I have elsewhere ventured to suggest that this stationary position of the mercury should not be taken as a decisive indication that the temperature of the solution has become constant; since I have found that the mercury, having once become stationary, remains so for any length of time during which the bulb experiences only slight changes of temperature, say a few ten-thousandths of a degree. Alas, this is the most troublesome way in which, what Abegg calls the «inertia» of these fine thermometers comes to light. It is for this reason that I have always been obliged to operate with a rising mercury column and that too with constant jarring, of great uniformity. In this way the errors arising from this source always lie on the same side and in measuring depressions of the freezing point would largely drop out. I have repeatedly observed this absolute constancy of the *mercury column* during a period of ten minutes, but the observation has never produced any feeling but that of despair, since it is reasonably sure that an absolutely constant *temperature* cannot be maintained for a period of ten minutes, to say nothing about three hours.



That the constancy of Abegg's *thermometer* is no certain test of the constancy of the *solution's* temperature but is due to «inertia», I think appears from an examination of a series of observations which he made on the freezing point of water (page 216). Eight such observations are published by him together with the barometric pressure at the time of each. Correcting these observations to a constant pressure by using the data which were obtained directly by experiment, we find that these eight determinations vary among themselves 0.005°C. This is more than ten times greater than the estimated error of the method. Abegg, however, is led to refer these great variations to *accidental impurities of the distilled water.* A moment's reflection shows that such supposed impurities would need to be so enormous that they would raise the water to the order of a 1/1000 normal solution at least, which would correspond to about 0.06 grams of sodium chlorid per liter! Since Abegg operated on salt solutions containing only a trifle more than twice this amount (0.00241-normal), we are forced to believe that he must have given some due attention to the preparation of suitable water for his work as well as taken the usual precautions for its protection against accidental contamination. One is the more safe in making this assumption since he gives the molecular strength of his dilute solutions to the fifth decimal or to a degree of accuracy a hundred-fold greater than his supposition in regard to the impurities of the water itself would permit.

It seems most reasonable to suppose, on the contrary, that these variations in the observations, great as they are, are to be referred jointly to the «inertia» of the thermometer, and the inability of the method to reproduce and maintain exactly the true freezing temperature of the water.

It may not be without value to call attention to the variations in the similar observations made with my thermometer (1893–1896).

The first series, extending over a period of five weeks, and comprising *sixteen* determinations, showed a maximum variation of 0.0015°C.[1] The second series, made during a period of twelve weeks, and comprising *twenty-five* determinations, show a maximum variation of 0.0038°C.[2] While a third series, not yet published, made during twelve weeks of the past winter and comprising *nineteen* determinations show a variation of 0.0030°C. It needs to be added that in this latest series the variation is of the nature of an almost uniform rise during the entire period. While the variations in my determinations of the freezing point of water appear thus to be about fourfold less than those of Abegg, I have never been able to believe that any measurable part of the variation could be referred to «accidental impurities» in the water itself. In fact, it is so desira-

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[1] Wied. Ann. **51**, 512 (1894).
[2] Ibid. **57**, 515 (1896).

ble to *know* that the water which I employed remained free from such accidental impurities that I have always measured periodically its *electrical conductivity* with this in view. Fortunately, I have thus far found no evidence of any accidental contamination of my stock of distilled water.

We should now seek a final answer in regard to the accuracy of the method by a direct examination of the results themselves. At the outset it is apparent that this accuracy is considerably greater in the new than in the old method. Inspection, however, of the results as exhibited by the curves in Figs. 1–8, for example in Fig. 1, where the results for NaCl are plotted, shows that much is still to be desired. If we suppose, as Abegg undoubtedly does, that the irregularities of this NaCl curve have no significance with reference to the solution itself at these points, but are to be referred to experimental errors, then we are obliged to admit that in the region $m = 0.022$ there is an experimental error of about *two hundredths* of a degree. Such errors must be assumed quite generally throughout the NaCl series as well as elsewhere in other solutions, in order to reduce the results to the required regularity. These errors are not to be explained by referring them to inaccuracy in the preparation of the solutions, though Abegg says this may amount to two per cent, since the total depression at $m = 0.022$ in the case of NaCl is only 0.0784° and an error of two per cent would still be less than 0.002°C, while the actual error here is something like ten times this amount. A study of these NaCl results together with those for grape sugar, Fig. 6, will require Abegg to agree with me in believing that his method has not yet reached a degree of accuracy which will justify its application to «very dilute solutions», and that the region of dilution beyond the 1/100 normal, while the most important of all, has as yet furnished few if any trustworthy results.

3. A careful study of the present method, independent of the results obtained by its use, leads one to regard it as entirely free from objections in principle; and convinces one that it marks a positive advance in freezing-point methods. The fact that Abegg's results do not justify this conclusion is not decisive against it. It seems certain if he will subject each solution to a number of entirely independent observations, that the average values will show little trace

of irregularity. I have always made five or more such independent determinations of each solution, and while the average *variation* in these series is not far from a full thousandth of a degree, the *mean values* thus obtained have never shown the slightest irregularity except in the region of extreme dilution. The work involved is great, but the method so carefully developed by Abegg warrants the belief that if this course is followed great increase in accuracy will result and important theoretical conclusions be established.

For the present the questions remain :—

Is the molecular depression in the case of non-electrolytes *constant*?

Or does it increase uniformly with increase of concentration?

Or does it exhibit a minimum value?

A decisive experimental answer to these important questions is most desirable. The persistent effort to perfect experimental methods of which the present one of Abegg marks a positive advance, warrants the hope that in the near future the difficult problems which this region of experimental Physics presents may be solved.

Princeton University.

SULFUR AND TOLUENE

BY J. K. HAYWOOD

At the request of Professor Bancroft I have made some determinations of the boiling points of mixtures of sulfur and toluene and of sulfur and xylene when there are present two liquid phases and vapor. The measurements were made in the old-fashioned Beckmann apparatus, using glass beads to ensure constant boiling. The thermometer was placed in the upper liquid layer, the one in which toluene is solvent. The toluene was carefully purified and boiled at 110°. On adding sulfur the temperature rose gradually to 112.05° and then remained constant. No attempts were made to determine the composition of the liquid phases at this temperature; but, by graphical interpolation from Alexejew's measurements, there should be thirty-three per cent of sulfur in one of the liquid phases and about ninety-two and one-half per cent in the other.[1] The xylene used had a boiling point of 138.95° while the monovariant system, sulfur in xylene, xylene in sulfur, and vapor, boiled at 143°, making a rise of boiling-point of about four degrees as against two in the preceding case.

In both these systems the constant boiling point for the two liquid layers and vapor lies between the boiling points of the two pure components. It is very easy to state the conditions under which this will occur. If a solid melts under a liquid with formation of a second liquid phase, there will be present at one temperature the nonvariant system, solid, two solutions and vapor. The vapor pressure of this system will be between the vapor pressures of the pure components or above that of either.[2] In the first case we

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[1] Wied. Ann. **28**, 310 (1886).

[2] This is on the assumption that the vapor pressure of the component which does not become solid is higher than that of the one which does.

shall have, at a temperature just above that of the nonvariant system, two liquid layers and vapor, the pressure lying between those of the pure components at that temperature. In the second case we shall have, at temperatures just below that of the nonvariant system, a saturated solution with a higher vapor pressure than the pure solvent. A mixture of naphthalene and water boils at a lower temperature than pure water and it is possible that at about 74° the saturated solution has a higher vapor pressure than pure water at that temperature. If not, there must be some temperature at which the two liquid layers have exactly the same pressure as pure water. Which of these two alternatives is the right one can only be settled by experiment ; but, at first sight, it would seem as if the former were the more probable. When a gas is dissolved in a liquid and the temperature rises, the solubility of the gas decreases and the difference between the vapor pressure of the solution and that of the pure solvent increases if the former be greater than the latter and decreases in the reverse case. When both components are liquids which become more soluble each in the other with rising temperature, it is to be expected that the vapor pressure of the solution will decrease relatively to the pressures of the pure components. The only case where this would not happen would be when the change of the solubilities with the temperature was small while the vapor pressure of the less volatile component increased enormously when compared with that of the other component.

Cornell University ; July 1, 1896.

NEW BOOKS

Vorlesungen ueber Gastheorie. *Ludwig Boltzmann. I. Theil: Theorie der Gase mit einatomigen Molekülen, deren Dimensionen gegen die mittlere Weglänge verschwinden. Large 8vo, vi and 204 pages. Leipzig. Johann Ambrosius Barth. 1895. Price, 6 marks.* The Kinetic Theory of Gases, as it stands to-day, constitutes one of the important applications of the theory of probability. This in itself is a sufficient explanation of the difficulty of the subject, of the controversies that have arisen over its fundamental principles, and of the aversion with which it is often regarded by the student. Within a few months one of the fundamental parts of the theory has been made the object of a vigorous onslaught by M. Bertrand, who declares it to be arrant nonsense, as he has so frequently done of other theories. The Kinetic Theory is important as being the only attempt to explain the fundamental properties of matter on a simple mechanical basis that has met with any success as to its agreement with the facts. That we should have such a theory for gases only is not surprising, in view of their simpler properties when compared with liquids and solids.

If the student anxious to gain a knowledge of the Kinetic Theory should ask where it is to be obtained we should immediately refer him to the various papers of Clausius, Maxwell, Boltzmann and Tait. If however he has not access to the numerous Transactions in which these have appeared, it will not be a difficult matter to name the available sources of information. The writer has before him on the table all the works with which he is acquainted that deal with the subject, and except for the two big volumes of Maxwell's papers they do not form a large pile. Of these only three are devoted exclusively to the Kinetic Theory. One only, the earliest as to date, is in English, namely the treatise of Watson. This deals almost exclusively with the establishment of a single theorem, that of Maxwell and Boltzmann on the distribution of the energy in the steady condition. The second, the treatise of O. E. Meyer, is valuable for the plain accounts of the principles involved and for the large collection of numerical data, the mathematical developments being crowded into an appendix. The third treatise, which constitutes the last volume of Clausius' *Mechanische Wärmetheorie*, is an account of the subject by one of its creators, and furnishes the student with an excellent idea of the essential parts of the theory, but is somewhat lacking in unity of treatment. Of works containing chapters devoted to the Kinetic Theory we may mention Maxwell's Theory of Heat, which treats the subject in a very elementary manner, without any reference to the theory of probability, Rühlmann's *Mechanische Wärmetheorie*, which contains an extended chapter on the subject, Voigt's *Kompendium der Physik*, which devotes a few brief pages to the matter, and Winkelmann's *Handbuch*, where we find an excellent chapter by Jäger. Finally, and best of all, we have Kirchhoff's *Theorie der Wärme*, of which the last eighty-six pages are devoted to the Kinetic Theory of Gases, the treatment being a very careful and lucid one, like everything that Kirchhoff ever wrote.

Christiansen's *Elemente der theoretischen Physik*, which treats such a great variety of subjects in such an interesting manner, has nothing at all on the Kinetic Theory.

In view of the small number of available text-books, the appearance of a treatise by Professor Boltzmann will be welcomed by many persons, especially if they have read his very interesting lectures on Maxwell's theory of electricity. Boltzmann is easily the first of living German theoretical physicists, and besides has contributed to the subject in question some of its most important parts. The present volume deals only with the simplest type of molecules, and therefore does not deal with the theorem especially connected with the name of Boltzmann, which concerns the partition of the energy among the various parameters that determine the state of the molecule, except in the particular case treated by Maxwell, where the parameters are the rectangular coordinates of the molecule. In the first section of the book the molecules are considered as small perfectly elastic spheres, in the second as point centers of repulsive force, and in the third the special assumption is treated making the law of the force that of the inverse fifth power, as suggested and developed by Maxwell.

The problem of the Kinetic Theory in its simplest case may be thus stated :—given a large number of equal small bodies flying about in a manner of which we know nothing, colliding with each other according to the principles of conservation of momentum and of energy, what fraction of the whole number will, after a great many collisions, possess any given velocity, how many collisions will there be, on the average, in a given time, how far will the particles travel, on the average, between two successive collisions, and in what manner will they carry from one place to another certain properties, such as mass, momentum, and kinetic energy. The first of these questions was asked and aswered by Maxwell. Of his law of distribution of velocities Maxwell gave two proofs. Of these the first is characterized by Kirchhoff as «*einfach, aber nicht streng*». It is, however, the only one usually given in the text-books. It depends only on the assumption that the probabilities of given values of the three rectangular components of the velocities of a molecule are perfectly independent. This assumption has been much criticized, and is the main object of Bertrand's attack. This proof is not given by Boltzmann, who gives what is substantially Maxwell's second proof. In this the effect of the collisions on the distribution of the velocities is considered, as it obviously must be. The steady state is declared to be reached when there is an exact equality between the number of collisions of two so-called opposite kinds. Boltzmann then goes on to consider the case where this equality is not observed, so that the state of the distribution varies with the time, with the result that a certain quantity **H** is shown to be continually diminishing. In the next section the quantity **H** is shown to have a simple relation to the probability of the distribution in question, so that the meaning of the «**H**-theorem» is that the distribution of velocities is continually tending towards the most probable distribution, which is that given by Maxwell's law.

From Maxwell's law immediately follows the equality of the mean kinetic energies of the molecules of two mixed gases in thermal equilibrium, and from this follows the law of Avogadro. It is remarkable that some of the principal results of the Kinetic Theory can be obtained without determining the distribution of velocities, for instance the laws of Boyle and Charles can be obtained even if we suppose all the molecules to have equal velocities. The simpler treatment is given by our author first, and afterwards the more complicated treatment involving the law of distribution. This method is pursued throughout the book, several theorems being proved in more and more complicated, but at the same time more strict, methods at various stages.

After the treatment of the specific heats of a gas the physical meaning of the quantity **H** is taken up, and in the case of the simplest kind of molecules, it turns out that—**H** differs only by an additive constant and a constant factor from the entropy. Accordingly the fact that the entropy can only increase appears as a theorem of probability. It is noteworthy that of the many attempts to found the second law of Thermodynamics on the laws of Mechanics, none has been successful, with the exception of this one for the case of a gas, and the cases treated by Helmholtz of monocyclic systems. This is not surprising, for we might expect that before obtaining the laws of phenomena by the laws of mechanics we must form some definite picture of the nature of the motions involved.

The next subjects in order are the number of collisions in a given time, and the mean free path. Here various opinions have prevailed as to the way in which the mean should be taken. These difficulties are of a mathematical nature, and are common to various questions of probability, and do not affect the physical reasoning. They seem after all hardly worth troubling one's self about, especially as the different methods affect the results only by slight numerical changes. Boltzmann, however, mentions the various definitions, although generally following those of Maxwell. Connected intimately with the mean free path are the questions of internal friction or viscosity, heat-conduction, and diffusion. These are all cases of the transportation of certain quantities mentioned above, and are interesting because of the knowledge that they give us as to the length of the free paths. The question of diffusion is probably the most complicated in connection with our theory, and has to be treated with certain approximations.

The student who has read the first section of the volume, already described, will have obtained a pretty good idea of the scope of the Kinetic Theory, and as he goes on will find still more careful treatments of similar matters. These partake somewhat of the nature of treatments of Hydrodynamics, mixed with the ordinary ideas of the Kinetic Theory, and follow in general the course of ideas of Maxwell's later papers, as does Kirchhoff also. Here we have an elaborate treatment of the entropy theorem, as well as a treatment of the behavior of a gas under the action of gravity. The last section of the book introduces the assumption that the molecules repel each other with a force proportional to the inverse fifth power of the distance. This is probably one of the least important portions of the theory, for the main results have been obtained otherwise. We find here, however, a rather important section on a generalized idea of entropy, with some instructive remarks on Dissipation of Energy.

In conclusion, the student desirous of studying the Kinetic Theory of Gases can hardly do better than take up this book, reading it slowly, and digesting every part before going on, confident that he will here find a clear and mathematically sound treatment of the subject, if one exists, «but that is another story.»

Arthur Gordon Webster.

Leçons de Chimie. *Henri Gautier et Georges Charpy. Second Edition, entirely recast. Large octavo, ix and 484 pages. Gauthier-Villars, Paris. 1894.* An elementary text-book for students in the Mathematical Course at the École Polytechnique, so the treatment is somewhat more mathematical than we are accustomed to find in our American text-books on Chemistry.

The present volume contains the general principles as a first part, and the metalloids as a second part, which compose the whole book so it is presumably followed by another volume containing the metals.

The first part contains an excellent theoretical sketch of those physical changes which play so important a part in chemical changes. Here the influence of Le Chatelier, who advised in the preparation, is seen. Unfortunately so much space is given to the writing of chemical equations and discussion of atomic weights and equivalents, that the reader gets the impression that just here algebra has been mistaken for chemistry.

In the second part the arrangement is according to the periodic law and the treatment of the subject is like that in any good American book. The book is up to date, argon and helium being considered; it is good but in no way original.

Clarence L. Speyers.

The Development of the Periodic Law. *F. P. Venable. 321 pages. The Chemical Publishing Co., Easton, Pa. 1896. Price $2.50.* An account of the origin and development not only of the periodic law, but of Prout's hypothesis, of the speculations on the genesis of the elements, and of the numerous attempts to represent algebraically or otherwise the relations existing between the atomic weights and the properties of the various elementary bodies.

The arrangement is chronological. Between two and three hundred books and papers are quoted and discussed, and the interest of the work is much increased by numerous reproductions of tables, diagrams and charts. In connection with the reprint *in extenso* of a few of the most important papers (Doebereiner, Pettenkofer, Meyer, Mendelejeff) in Ostwald's *Klassiker*, Nos. 66 and 68, the present work renders easily accessible a vast mass of literature dealing with this important subject, most of which has hitherto been hidden in obscure publications or scattered through the various scientific journals from 1815 to the present day.

In dealing with the inception of the periodic law, the author protests against the prominence given by Lothar Meyer to the work of Pettenkofer. He is of the opinion that «while Pettenkofer undoubtedly gave expression to some of the ideas contained in Dumas's Ipswich address rather more than a year before this address was delivered, it is equally certain that his paper did not follow the train of thought nor contain the brilliant speculations which attracted the attention of the world to the address of Dumas. For eight years Pettenkofer's work was practically unknown, while Dumas's had proved an incentive to a band of earnest workers, and was really the cause of Pettenkofer's republication».

The book is brought up to date by reviews of papers published in the current year, and is completed by a bibliography of no less than 267 titles, a list of authors, and a very full general index.

W. Lash Miller.

A Manual of Physics. *W. Peddie. 2nd Edition. viii and 357 pages. G. P. Putnam's Sons. New York. 1896. Price $2.50 nett.* In this second edition the author has dispensed with the services of the calculus, and has employed mathematical methods of the ‹elementary› description only; by making repeated use of the same mathematical devices throughout the book, he has succeeded in avoiding some at least of the disadvantages consequent on this method of treating the subject.

In order to give «as complete a view of the essential unity and interdependence of the various branches of the subject» as possible there are introduced among the chapters on motion, sound, light, heat, electricity and magnetism into which the work is divided, articles on «The Physical Universe», «Methods of Physical Science», «the Basis of Physical Belief», *etc.;* while with the purpose of «bringing into prominence the necessity for and the value of scientific hypotheses—a matter regarding which very hazy notions are only too common» twenty-five pages are devoted to an account of the molecular theory, a short chapter to ‹the ether›, and another to the electromagnetic theory of light; and the theory of energy is illustrated not only by the article on thermodynamics but by a special chapter on ‹related physical quantities›. This latter chapter is of peculiar interest to the student of physical chemistry as it is largely owing to the successful application of the theory of energy to problems within his own province, that the importance of the methods involved has come to be generally recognized. It is probable however, that the leaders in this department of science would be the very last to give their assent to Dr. Peddie's proposition, that the basis of the second law of thermodynamics is—the molecular constitution of matter!

The author has apparently considered it beyond the scope of his ‹manual› to give any account of the recent advances in those departments of Physics to which the attention of the chemist has been of late more particularly directed. In the chapters on electricity, for instance, the book has been brought up to date by an account of Hertz's electric waves, but no mention is made of the work of Hittorf, Kohlrausch and Arrhenius on the electrolysis of solutions; Grotthus's antiquated theory is given, and illustrated by a diagram; and Faraday's law is stated incorrectly. The subject of Osmosis is disposed of in twenty lines, dissociation and chemical combination in twenty-five, and though the sections on molecular theory begin with Lucretius and include an account of the vortex-atom, no mention is made of the important extension of that theory necessitated by the work on solutions carried out within the last ten years.

W. Lash Miller.

Notes on Qualitative Analysis, for Students of the Rensselaer Polytechnic Institute. *W. P. Mason. 3d Edition. Chemical Publishing Co. Easton, Pa. 1896. Price 80 cents.* «The market is unquestionably much overstocked with books upon this subject, and the author's only excuse for making the addition to the number is that it meets the requirements of his own classes.

There is small doubt that were it not for the expense of printing, every teacher of chemistry would use a text book made by himself with either pen or scissors, . . . the attempt has been made in those notes to induce the student to make use of works of reference. . . It is hoped . . . what is here given may . . . create a desire to know rather than a desire to pass.

It is to be regretted that the energies of the student are so often bent towards blindly following the words of the text. . .» Is it in order to avoid this propensity on the part of his readers that the author, following a time-honored custom—has provided them, at the end of his volume, with such a convenient set of tables for complete analysis? If so he may rest assured of a certain measure of success, for it is surely the general experience that this arrangement renders it difficult to persuade the ordinary ‹student› to read the words of the ‹text› at all! *W. Lash Miller.*

Elektrometallurgie. *W. Borchers. Second Edition. Large octavo, viii and 393 pages. H. Bruhn. Braunschweig, 1896. 14* *marks, bound 16 marks.* The author has given a very complete account of the applications of electricity to the preparation of metals,—including electrical heating as well as electrolytic processes under this head. In addition he has described many futile inventions, showing the faults in each. To the student this part of the book will be especially valuable. The training of the modern chemist is singularly defective from a practical point of view. The difficulties, which a manufacturer has to meet, are rarely problems which have already been worked out in the books. For this reason, what the technical chemist needs is not a vast accumulation of facts but a great deal of common-sense and an ability to apply general principles to particular cases. At present, men in the Universities make some organic preparations and then spend several years upon researches in which the aim is to isolate and analyze new compounds, little or no attention being paid to improving the methods. It is doubtful whether such a training has any scientific value, but it is admirably calculated to unfit a man for making a success in life. There is a crying need for a book on theoretical organic chemistry which will do what this book of Borchers does for practical metallurgy. A student who should invent successively the different processes described by Borchers would find that he had acquired a remarkable power to solve problems.

Passing from the student to the manufacturer, a single instance will suffice to show the assistance which this book might be to mining companies. It is reported that the Anaconda Company has recently put in a large plant for the Thofehrn process, while we learn from Borchers that this process cannot be considered the latest or best method of obtaining copper electrolytically.

Wilder D. Bancroft.

Les applications de l' électrolyse à la métallurgie. *M. U. Le Verrier. Small octavo, 56 pages. Gauthier-Villars et fils. Paris. 1896.* This pamphlet gives an elementary account of some of the newer processes in electrometallurgy. Thirty-six pages are devoted to the methods of obtaining copper by electrolysis with incidental remarks upon current, electromotive force, impurities and the question of cost. In the remaining twenty pages reference is made to the electrolytic separation of nickel, zinc, antimony, tin, silver and gold. It is a pleasure to note that the author is familiar with the recent work published in German and English.

Wilder D. Bancroft.

The Gases of the Atmosphere. *The History of their Discovery. William Ramsay. Small octavo, viii and 240 pages, with eight portraits. The Macmillan Co. New York, 1896. Price $2.00.* The discovery of a new chemical element is from its very nature of more popular interest than most other pieces of pure scientific research even if the new element is almost devoid of chemical properties, but aside from this fact, the appearance of this book by Professor Ramsay, written in popular style, is amply justified from the fact that it presents in detail a superb example of the methods of modern chemical investigation, as contrasted with the older and cruder methods. And it is very fitting that an historical account of the discovery of the other gases in our atmosphere should lead up to the main subject.

The volume is timely, and the matter clearly and logically treated. The first half of the book is taken up with the discoveries of carbon dioxid, nitrogen, oxygen, hydrogen, the composition of water and of the atmosphere, interspersed with short biographical sketches. Then comes the well known discovery of argon by Lord Rayleigh and Professor Ramsay.

Perhaps the most interesting parts of the book are the last chapters upon the physical properties of argon and its place in the scheme of the chemical elements. Here are given the experiments and the reasons therefrom for the conclusion that it, like mercury, is monatomic, and that it is not a mixture of two elements. The fact is mentioned that the most trustworthy value obtained for the ratio of the specific heats might allow the presence of about two per cent of diatomic molecules, but upon the whole, the presumption is against such a mixture.

As to the fact that there seems to be no fit place for argon in the periodic table the author brings forward the suggestion that it may not be impossible that the presence or absence of intense chemical properties may have some effect upon the mass of elements as determined by their weights, and refers to the experiments of Airy and of Landolt.

A volume such as this, designed for readers not especially familiar with the technicalities of the science, has worth only when in the treatment of the subject there is combined with clearness and lucidity, accurate scientific methods of treatment, and the above work certainly falls into this class. It is eminently scientific.

The book is well printed on good paper and the portraits of the older chemists make it more attractive.

One slight error was noticed. On page 225 the freezing point of chlorin is used for the boiling point, (— 102° for — 33.6°) and this necessitates a numerical change in line one of the following page.

G. W. Coggeshall.

Annuaire pour l' an 1897, publié par le Bureau des Longitudes. In-18, v and 918 pages, with two Magnetic Maps. Gauthier-Villars et fils, Paris. Price 1.50 francs. In addition to the great mass of physical and astronomical data which it contains every year the *Annuaire* of the *Bureau des Longitudes* for 1897 presents articles written by prominent men of science on Finance, Statistics, Geography, Mineralogy, *etc.*, among which may be specially noted the following: Note upon the Proper Motion of the Solar System, by M. F. Tisserand; Cathode Rays and Röntgen Rays, by M. H. Poincaré; The Epochs in the Astronomical History of the Planets, by M. J. Janssen; Note on the Fourth Meeting of the International Committee for the Execution of a Photographic Map of the Heavens, by M. F. Tisserand; Note on the Labors of the International Commission for Fundamental Stars, by M. F. Tisserand; Address delivered at the Funeral of M. H. Fizeau, by M. A. Cornu; Address delivered at the Funeral of M. Tisserand, by MM. H. Poincaré, J. Janssen, and M. Loewy; Investigations at Mont Blanc in 1896, by M. J. Janssen.

REVIEWS

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

General

Remarks upon the Analytical Representation of the Periodic System of the Elements. *A. Goldhammer. Phil. Mag.* **42,** *277* (*1896*). The author endeavors to represent by a curve the «positivity» of the elements as a function of their atomic weights. He then points out that for each value of the valency the properties of the elements vary periodically with increase in the atomic weight, and discusses the consequences of the assumption that these two periodic functions are independent of each other. If they prove to be so, then for each value of the valency, there must be a completely determinate series of atomic weight values, representing the atomic weights of the elements actually existing. In conclusion the author expresses the opinion that the cotangent formula of Flawitzky and J. Thomsen is probably not complicated enough to represent the actual relationships. *W. L. M.*

A Convenient form of Measuring Flask. *W. Wislicenus. Ber. chem. Ges. Berlin,* **29,** *2442* (*1896*). The modification suggested by Biltz [*Ber.* **29,** *2082* (*1896*); *this Journal* **1,** *185*] has been in use since 1886. The writer recommends the flasks with *two* marks, one above and one below a 100 *c.c.* bulb in the neck, which are made by Geissler (Bonn) and contain two, one, and one-half liters respectively. *W. L. M.*

A new Machine for shaking Bottles, etc. *M. v. Recklinghausen. Ber. chem. Ges. Berlin.* **29,** *2372* (*1896*). Illustrated description of a simple piece of apparatus driven by a water turbine. By reducing to a minimum the surfaces at which friction occurs, the inventor has sought to simplify the construction to lessen the power required, and to avoid the evil effects of the laboratory atmosphere. For sale by C. Desaga, Heidelberg. *W. L. M.*

On the Dependence of the Formation of Glycerol upon the Conditions of Fermentation. *Address by Dr. Kulisch. Zeit. angew. Chem.* **1896,** *418.* It has been supposed that glycerol is produced in wine in proportion to the quantity of alcohol present. This is shown to be wrong, the production is increased by all factors—of feeding, *etc.*—which favor the growth of the ferment.

J. E. T.

On a New Determination of the Mass of a Decimeter of Air-free Distilled Water at its Maximum Density. *J. Macé de Lépinay. Jour. de Phys.* (*3*) **5**, *477* (*1896*). The result is 999.959 grams, supposed to be exact to within about six milligrams.

J. E. T.

On the Life and Work of Louis Pasteur. *A. Fernbach. Bull. soc. chim. Paris.* (*3*) **15**, *No. 15, I* (*1896*). Apart from its appreciative account of Pasteur's career the present article is especially valuable for an appended bibliography of Pasteur's writings,—a list occupying eleven pages. *J. E. T.*

Lothar Meyer Memorial Lecture. *P. P. Bedson. Jour. Chem. Soc.* **69**, *1403* (*1896*). An appreciative review of Meyer's life and work, delivered before the Chemical Society of London.

J. E. T.

Revision of the Atomic Weight of Magnesium. *T. W. Richards and H. G. Parker. Zeit. anorg. Chem.* **13**, *81* (*1896*). For $O = 16.00$ the atomic weight of magnesium is found to be: $Mg = 24.362$. *W. D. B.*

Action of Silicon on the Alkaline Metals, Zinc, Aluminum, Lead, Tin, Antimony, Bismuth, Gold and Platinum. *E. Vigouroux. Comptes rendus,* **123**, *115* (*1896*). Of these metals only platinum combines with silicon. The compound has the formula $SiPt_2$. *W. D. B.*

Relation among the Atomic Weights of Elements. *Delauney. Comptes rendus*, **123**, *600* (*1896*). The author divides the elements into five classes. In four of these classes the atomic weights can be represented by the four formulas: $12 + 4x$, $7 + 4x$, $2 + 4x$, $9 + 4x$. In these formulas x is never fractional. In the fifth class are placed all elements not otherwise accounted for. *W. D. B.*

Uniformity of the Distribution of Argon in the Atmosphere. *T. Schloesing. Comptes rendus*, **123**, *696* (*1896*). Samples of air were taken at different points between the Azores and the English Channel. The maximum variation in composition is less than four parts in a thousand parts of argon. *W. D. B.*

Addition to the Paper: On «Thermometers with Varying Amounts of Mercury». *F. Grützmacher. Zeit. Instrumentenkunde*, **16**, *200* (*1896*). The author has determined and tabulated the corrections to be applied to the Beckmann thermometer at different temperatures. Errors up to five percent may be introduced by neglecting this correction. *W. D. B.*

Mercuric Chlorothiocyanate. *C. H. Herty and J. G. Smith. Jour. Am. Chem. Soc.* **18**, *906* (*1896*). Mercuric chlorothiocyanate, $HgCl(CNS)$, is decomposed by water with precipitation of mercuric thiocyanate. *W. D. B.*

Researches on Double Cyanids. *R. Varet. Comptes rendus*, **123**, *118* (*1896*). Equivalent solutions of the cyanids of the alkaline metals and alkaline earths give the same heat effect with silver cyanid; also with nickel cyanid. *W. D. B.*

Thermochemical Researches on Cyanamid. *P. Lemoult. Comptes rendus*, **123**, *559* (*1896*). In aqueous solution cyanamid acts like a monobasic acid. The heat of neutralization is 3.6 cal. *W. D. B.*

Researches on Double Chlorids. *R. Varet. Comptes rendus*, **123**, *421* (*1896*). Thermochemical data in regard to the formation of double chlorids in aqueous solution. *W. D. B.*

Researches on Double Bromids. *R. Varet. Comptes rendus*, **123**, *497* (*1896*). Thermochemical data for the action of mercuric bromid on other bromids in solution. *W. D. B.*

On the Heat of Formation of Lithium Hydrid. *Guntz. Comptes rendus,* **123**, *694* (*1896*). Thermochemical data.

W. D. B.

Hexamethylenamin and its Nitroso-derivatives. *M. Delépine. Comptes rendus,* **123**, *650* (*1896*). Thermochemical data.

W. D. B.

Monovariant Systems

On the Complete Calorimetric Study of Saturated Liquids. *E. Mathias. Jour. de Phys.* (*3*) **5**, *381*, (*1896*). A liquid in presence of its saturated vapor is completely known from a calorimetric point of view when we know the internal and external heats of vaporization, ρ and γ, the specific heat of the liquid under the pressure of its vapor m, and the specific heat of the saturated vapor, m'. Hitherto m' has always been found from the equation

$$m' = m + \frac{d\lambda}{dT} - \frac{\lambda}{T}$$

where $\lambda = \rho + \gamma$. The present paper contains an experimental study of m, m' and ρ. The method has been described in previous papers C. r. **119**, *404 and 849* (*1894*). It assumes a complete preliminary study of the vapor pressure, vapor density and density of the saturated liquid at all temperatures up to the critical point. A copper vessel is charged with SO_2, heated to a known temperature and plunged into a calorimeter. A series of such experiments is performed with smaller and smaller amounts of SO_2. By the aid of equations previously deduced (C. r. **119**, *849*) it is possible to find from one series of experiments m, m' and ρ.

For SO_2, m' which is negative for ordinary temperatures increases through 0 at 97.5° and reaches a maximum at about 106°, after which it decreases through 0 at 114° to $-\infty$ at 156°, the critical temperature. On the contrary m has no maxima, minima or points of inversion but increases regularly to $+\infty$ at 156°. If δ and δ' are the densities of the liquid and the vapor, $\rho/(\delta - \delta')$ is very nearly constant in confirmation of a rule already announced by Bakker.

E. B.

A Contribution to our Knowledge of Explosions. *C. Hoitsema. Zeit. phys. Chem.* **21**, *137* (*1896*). The paper consists of some reflections on the connection between temperature and explosions. The conclusion was that by careful regulation of temperature it should be possible to make the explosive body react very slowly until it entirely disappeared. The products of the slow reaction need not be identical with the products of the explosive reactions. The conclusion was supported by experiments on silver oxalate, sulfur nitrid (S_4N_4), mercury fulminate, silver fulminate.

Silver oxalate decomposed slowly into $2Ag + 2CO_2$, no CO being formed, so that the slow reaction gave the same products as the explosive reaction.

Sulfur nitrid gave the same products in the slow reaction as in the explosive reaction; namely, $4S + 2N_2$.

Mercury fulminate gave different products in the two reactions. When exploded it gave $Hg + 2CO + N_2$; when decomposed slowly, it gave off almost pure O_2, the solid residue seemed to be mercuric oxid with paracyanogen (?).

Silver fulminate behaved like mercury fulminate.

C. L. S.

Investigation to determine whether Diphenyliodonium and Thallium Nitrates are Isomorphous. *A. A. Noyes and C. W. Hapgood. Technological Quarterly*, **9**, *236*; *Chem. News* **74**, *217* (*1896*). V. Meyer has observed great similarity in the properties of the salts of diphenyliodonium $(C_6H_5)_2I{\cdot}OH$ and of thallium, it was therefore of interest to seek whether they be isomorphous. Saturated solutions of the nitrates in aqueous solutions of the free base were mixed in varying proportions and evaporated; determination, by the method of Retgers, of the densities of the crystals formed showed that the two salts crystallized separately, they are therefore not isomorphous. *J. E. T.*

On the Freezing Point of Dilute Solutions. *Ponsot. Jour. de Phys.* (*3*) **5**, *337* (*1896*). Abstract of book reviewed in this Journal, **3**, *178*. *J. E. T.*

Absorption of Dilute Acids by Silk. *J. Walker and J. R. Appleyard. Jour. Chem. Soc.* **69**, *1334* (*1896*). If the concentration of picric acid in aqueous solution be W and in dyed silk S the formula

$$\log S + 2.7 \log W = \textit{constant}$$

describes the experimental results with sufficient accuracy. Since the reacting weight of picric acid in the aqueous solution cannot be greater than its reacting weight in silk the authors conclude that a solid solution is not formed. All that the experiments really show is that Nernst's Distribution Law does not apply without modification. Picric acid and diphenylamin form a compound and the concentration of picric acid in aqueous solution is constant so long as solid diphenylamin and diphenylamin picrate are present. This is predicted from an application of the Mass Law; but it is really a case described by the Phase Rule since there are three components and four phases. Picric acid in alcoholic solution dyes silk; but silk will not absorb the dye from benzene nor will benzene remove picric acid from silk. Experiments with dilute acids in aqueous solution showed marked effects due to electrolytic dissociation and to the nature of the acid. *W. D. B.*

On Metallic Alloys. *H. Gautier. Comptes rendus.* **123**, *172 (1896)*. The freezing points of mixtures of copper and nickel imply the existence of two sets of solid solutions; cadmium and silver show a similar curve though not so clearly marked. With zinc and silver the order of crystallization is probably solid solution and then silver. Tin and antimony give normal though unusually wavy curves with silver. *W. D. B.*

On the Fusibility of Metallic Alloys. *H. Gautier. Comptes rendus*, **123**, *109*, *(1896)*. The freezing points were determined of mixtures of tin and nickel, tin and aluminum, aluminum and silver, antimony and aluminum. In all cases addition of the less fusible metal lowered the freezing point; but this portion of the curve is so short, except in the silver-aluminum series, as to make it doubtful whether pure solvent crystallizes. The only compound formed is Ag_3Al, stable at its melting point. In all the other systems maximum temperatures were observed; but these are probably points where the liquid and solid solutions have the same composition. With antimony and aluminum there are two such points, both occurring at temperatures above the melting point of either of the components. The antimony fused at 632° and must have been the amorphous modification. *W. D. B.*

The Diamonds in Steel. *Rossel. Comptes Rendus.* **123,** *113* *(1896).* Since Moissan has shown that carbon crystallizes under pressure from iron as diamond, it seemed probable that hard steel contains microscopic diamonds. Analysis shows this to be the case.
W. D. B.

Researches on the Behavior of Nitrobenzene as Solvent in Cryoscopic Experiments. *G. Ampola and E. Carlinfanti. Gazz. chim. Ital.* **26,** *II, 76 (1896).* The mean of the constants for thirteen solutes which gave normal depressions in nitrobenzene is 69.07. The value calculated from the heat of fusion is 68.6.
W. D. B.

Parabromtoluene and Veratrol as Solvents in Cryoscopic Experiments. *E. Paternò. Gazz. chim. Ital.* **26,** *II, 1, 9 (1896).* The constant for parabromtoluene is 82.1 and for veratrol 63.8.
W. D. B.

New Observations on the Cryoscopic Behavior of Substances having a Structure Formula similar to that of the Solvent. *F. Garelli. Gazz. chim. Ital* **26,** *II, 380 (1896.)* The substance C_5H_6 gives normal values in paraxylene, abnormal ones in benzene. The polymer $C_{10}H_{12}$ gives normal values in benzene, naphthalene, diphenyl and phenanthrene. Fluorene gives normal values in benzene and naphthalene; but raises the freezing points of solutions in which phenanthrene is solvent.
W. D. B.

New Studies on the Behavior of Phenol as Solvent in Cryoscopic Experiments. *E. Paternò. Gazz. chim. Ital.* **26,** *II, 363 (1896).* Twenty solutes were studied and the range of concentrations was unusually extensive. Alcohols and phenols gave very constant values. In all other cases the variations with increasing concentration were fairly large. *W. D. B.*

Influence of the Temperature of the Freezing Mixture upon Cryoscopic Measurements. *F. M. Raoult. Zeit. phys. Chem.* **20**, *601*, (*1896*). The author deduces the formula of Nernst and Abegg for the relation between the apparent and the true freezing point and advises determining the constant in the equation by making several measurements of the apparent freezing point with the freezing bath at different temperatures. When the bath is three degrees below the freezing point, the stirrer revolves five times per second and the solution is supercooled half a degree, the author finds that the difference between the apparent and the true freezing point is from one to five one-thousandths of a degree depending on the nature of the solute. *W. D. B.*

On the Determination of the Freezing Point in Dilute Aqueous Solutions. *A. Ponsot. Comptes rendus*, **123**, *189* (*1896*). The author objects to Raoult's assumption that the difference between the apparent and the true freezing point is proportional to the concentration.

W. D. B.

On the Solubility of Lead and Bismuth in Zinc. *W. Spring and L. Romanoff. Zeit. anorg. Chem.* **13**, *29* (*1896*). The authors determined the solubility curves for lead and bismuth in zinc and for zinc in lead and bismuth. Zinc and bismuth become consolute at about 825°, zinc and lead above 900°.

W. D. B.

Accurate Cryoscopic Measurements. *Reply to F. M. Raoult. A. Ponsot. Comptes rendus*, **123**, *557* (*1896*). The author states that the ideal conditions for accurate measurements are that there should be no radiation of heat and a minimum amount of stirring. He also complains that Raoult has not replied to the theoretical criticisms and that Raoult's experimental data prove nothing. There seems to be a confusion in the author's mind between the ideal conditions for equilibrium and the ideal conditions for determining that equilibrium—two very different things.

W. D. B.

Accurate Cryoscopic Measurements; Applications to Solutions of Sodium Chlorid. *F. M. Raoult. Comptes rendus*, **123**, *475*, *631 (1896)*. The author shows that with sodium chlorid solutions, his formula for the real freezing point describes the facts. For infinite dilution he finds K = 37.82 corresponding exactly to the theoretical value for complete dissociation. He claims that Ponsot's measurements are inaccurate owing to insufficient vertical stirring.

W. D. B.

The Alkali Trihalides. *C. H. Herty and H. V. Black. Am. Chem. Jour.* **18**, *847 (1896)*. It is shown that rubidium iodid passes over into the salt $RbBr_2I$, when treated with bromin and that no solid solution is formed. Mr. Herty's work upon double salts has been so excellent as far as it goes that it is a great pity he does not make it a little more comprehensive. The day is past when it is sufficient to analyze the solid phases; one wishes also to know at what concentration for a definite temperature the solid phase appears.

W. D. B.

Divariant Systems

The Viscosity of Mercury Vapor. *A. A. Noyes and H. M. Goodwin. Phys. Rev.* 4, *207, (1896)*. Recent discussion concerning argon and helium has shown that the ratio of the specific heats is not regarded as conclusive evidence upon the atomicity of the molecule. The authors undertake, therefore, to investigate some property which depends on the cross section of the molecule and choose viscosity as the subject of their experiments. According to the kinetic theory of gases

$$\frac{q_1}{q_2} = \frac{\eta_2}{\eta_1}\sqrt{\frac{m_1}{m_2}}$$

where q_1 is the cross section of the molecule, η_1 the coefficient of viscosity and m_1 the molecular weight of the first gas, and q_2, η_2, m_2 the corresponding quantities for the second gas.

The gases compared were mercury, hydrogen and carbon dioxid. They were sucked through a capillary tube kept in the vapor of mercury boiling at atmospheric pressure. Experiments were made with two different capillaries and the agreement of the results was satisfactory. The values of η found from the observations gave $q_{Hg}/q_{CO_2} = 1.02$ and $q_{Hg}/q_{H_2} = 2.48$. «These results indicate that *atoms and molecules are of the same order of magnitude*, and that the spaces between the atoms within the molecule, if any exist, are not large in comparison with those occupied by the atoms themselves. And, consequently, the viscosity of gases or any other property which, like it, is dependent only on the size or form of the molecules is not adapted for distinguishing between monatomic and polyatomic molecules».

The authors fail to notice that the «uncertainty» of the specific heat method is due to the fact that the whole kinetic *theory* is pure *hypothesis* so that at the first difficulty faith in its conclusions begins to waver and attention must be distracted from points where the theory is obviously useless to others where hope is still permissible.

E. B.

The Specific Heats of the Metals. *F. A. Waterman. Phys. Rev.* 4, *161* (*1896*). After a preliminary discussion of the defects of the ordinary calorimetric methods, especially those of the Bunsen ice-calorimeter method which is commonly assumed to be very accurate, the author described his improvements on the method of Hesehus. The advantage of this method is that corrections for cooling and for the water equivalent of the calorimeter are avoided by keeping the calorimeter constantly at the temperature of the room. To insure detection of any inconstancy in temperature the calorimeter, a silver test tube, is enclosed, after the manner of the inner vessel of Bunsen's ice-calorimeter, in the bulb of an air thermometer. Kerosene was used as the manometric fluid, and the air thermometer was sensitive to 0.01°C. The body to be investigated is heated in an electric heater which can be swung about a vertical axis so as to come above the calorimeter. The body is lowered by a thread into the calorimeter which contains enough water, previously weighed, to cover the body, the whole calorimeter with the water being at room temperature. The heater is then swung aside and in its place there is introduced an apparatus for dropping into the calorimeter cold water which is run in just fast enough to prevent any change in the reading of the air thermometer. A final weighing of the silver tube and its contents gives the weight of cold water used. This, with the weight of the solid body and the temperatures of heater, cold water and room, gives the data for finding the specific heats. The specific heats found for the six metals used were Bi 0.03035; Sn 0.05453 ; Al 0.21946 ; Cu 0.09471 ; Au 0.03068 ; Zn 0.09547. The method seems to give very accurate results, the probable error of the results given being about ±0.04 per cent. Tables are given of the specific and atomic heats of all the metals, so far as those are known, the tables being based on what the author considers the most reliable data, including his own. A useful list of references completes the paper which seems to the reviewer a valuable addition to the literature of calorimetry. *E. B.*

The Solution of Liquids and Solids in Gases. *P. Villard, Jour. de Phys.* (*3*) **5**, *453* (*1896*). The author describes his experiments on various two-phase systems when the phases are a gas and a solid or a gas and a liquid. At constant temperature an increase of pressure increases the mutual solubility and the phases approach equal composition which is reached for a certain critical pressure at which the surface of demarcation vanishes. The phenomena are similar to those at the critical state of a single substance. If the tube containing the system is not shaken, the phases do not become homogeneous except by a very slow diffusion but the sharp surface is replaced by a zone of continuous change. The gases used were O_2, H_2, air, formene, ethylene, CO_2 and NO. Among the solids and liquids used were Br, I, CS_2, C_2H_5Cl, camphor and paraffine. The temperatures used were that of the room (17°±) and in a few cases 150°. The pressures went up as high as 550 atmospheres. The article ends with a section in which the author discusses, with reference to the phenomena mentioned above, the influence of a so-called indifferent gas on the density of the gaseous dissociation products of a solid. *E. B.*

The Thermodynamic Surfaces of a Body in the Solid and Liquid States. *G. Tammann. Zeit. phys. Chem.* **21**, *17* (*1896*). The author proposes to use Ω, v, t, instead of p, v, T, in constructing thermodynamic surfaces. The symbol Ω represents the outward pressure resulting from the kinetic energy of the molecules; it is connected with p by the equation $\Omega = K + p$, where K is the molecular attraction [$K = \frac{a}{v^2}$ of van der Waals? R.] directed inwards as p is. By so doing the breaks in the thermodynamic surfaces constructed with p, v, T, are much modified and perhaps can be made to disappear entirely, though it is not probable that the transition from liquid to vapor through overheated liquid and undercooled vapor can be made in a gradual way ; the outlook is more promising, however, in the transition from solid to liquid.

The data for testing the value of the proposal are very meagre. The few qualitative comparisons possible for the isothermal of naphthalene as obtained by Barus were satisfactory ; likewise the isobars of a number of bodies gave satisfactory qualitative results.

The paper closes with an instructive discussion of the equation

$$\frac{dT}{dp} = \frac{T}{Q}(v' - v'')$$

where v' is the volume of a unit mass of liquid, v'' that of the solid, Q the heat of fusion, dp the increment in fusion pressure corresponding to dT the increment in fusion temperature, and T the absolute fusion temperature.

[The reviewer cannot see anything more in the proposal than to substitute for the well known insufficient p the sufficient quantity $p + \frac{a}{v^2}$, of van der Waals].

C. L. S.

On the Influence of the Chemical Constitution of Organic substances on their Ability to form Solid Solutions, *III. F. Garelli Zeit. phys. Chem.* **21**, *113* (*1896*). In determinations of the freezing points of solutions of cyclopentadien in benzene and of fluorene in phenenthrene, the author finds further confirmation of his generalization that «organic substances whose structural formulae contain similar rings of atoms, without side chains, may form solid solutions with each other» [*Zeit. phys. Chem.* **13**, *4* (*1894*)].

In spite of this connection between constitution and miscibility which he has discovered, Garelli is fully aware that in many cases substances crystallize together that have neither similar constitutions nor similar crystalline forms,—he has already, indeed, had occasion to insist on this point [*Zeit. phys. Chem.* **18**, *59* (*1895*)] in view of some «very superfluous» remarks of Beckmann's on his work—and in the present paper he refutes Küster's opinion, that in every case ‹solid-solutions› are nothing but isomorphous mixtures, by giving the crystallographic constants of the substances employed in his experiments. *W. L. M.*

On the Determination of Molecular Weights, *IV. E. Beckmann. Zeit. phys. Chem.* **21**, *239*, (*1896*). A short article on the use of pure solvents in boiling-point determinations, and an illustrated description of

1. A freezing-point apparatus with electromagnetic stirrer for use with hygroscopic solvents; the interruptions in the electric current actuating the stirrer are effected by a simple apparatus made out of a metronome. To introduce difficultly soluble substances, a basket of platinum gauze may be employed.
2. An air mantle and a modified form of condenser for the boiling-point apparatus. Platinum foil rolled together and cut with the scissors into small tetrahedra is recommended in place of garnets, glass beads, *etc.*
3. The proper form of reservoir for Beckmann's thermometer, to keep the mercury attached to the capillary.

W. L. M.

On the Increase of Volume attending the Solution of Ammonium Salts and of Sodium Thiosulfate. *H. Schiff and U. Monsacchi. Zeit. phys. Chem.* **21**, *277* (*1896*). Measurements of the specific gravities of the salts mentioned below, and of their solutions in water. The volume of the solutions of ammonium nitrate, chlorid and bromid is greater than that of the dry salt and water from which they are formed; that of ammonium iodid and hydrazin chlorid is less; while in the case of hydroxylamin chlorid and sodium thiosulfate, the volume of dilute solutions is less, that of concentrated greater, than that of their components.

If ammonium nitrate be dissolved in aqueous nitric acid, or in solutions of potassium nitrate or of ammonium chlorid, the expansion is greater than when pure water is used; if the water be imagined as divided between the two salts in the proportion of their solubilities, the volume of the solution may be approximately calculated. If alcohol be employed as the solvent, the contraction is greater than with water (ammonium nitrate, iodid).

W. L. M.

On the Heat of Solution of Sodium Chlorid. *E. von Stackelberg. Zeit. phys. Chem.* **20**, *159*, (*1896*). Making use of older work of Winkelmann (1873) and of Staub (1890), together with new measurements of his own, the author has constructed two sets of curves. I: For the heats of solution (heat absorbed) of sodium chlorid in NaCl-solutions of concentrations rising from zero to saturation at 35.52g in 100 of water,—one curve each for 0°, 18° and 50°. The first two curves cut the saturation ordinate at —4 cal and +1.2 cal respectively, so at 0° the heat of solution in saturated solution is negative and at 18° it is positive, the solubility first falls with rising temperature, passes through a minimum and then rises. These two curves intersect near the abscissa for 20g salt in 100 of water, so for more dilute solutions the temperature of the coefficient of the heat of solution is negative, for more concentrated ones it is positive. This is also true of $NaNO_3$, KNO_3, KCL and NH_4Cl in water.

The second set of curves, II: gives the total heats of solutions, from zero up to the different concentrations,—three curves for the same three temperatures. The 0°-curve shows a maximum near the concentration of twenty-five per cent, corresponding to the change of curve I, for the same temperature and concentration, from positive to negative values.

J. E. T.

General Theory of the Fluid State. *H. K. Onnes. Arch. néerl.* **30**, *101* (*1896*). This paper is a reprint of a memoir published by the Amsterdam Academy in 1881, it is an extension of the van der Waals's molecular-kinetic theory of vapors and of continuity.

J. E. T.

The Kinetic Interpretation of the Thermodynamic Potential. *J. D. van der Waals. Arch. néerl.* **30**, *137* (*1896*). Calculations from van der Waals's equations of condition as a basis, to show for a single substance and a mixture of two substances how kinetic considerations can lead to results previously reached more simply and more generally by the method of pure thermodynamics. It is demonstrated in particular that when two components are in equilibrium in two coexisting phases the one requiring the greater expenditure of work in passing from one phase to another is present in greater relative amount in the first of the two phases. If both phases have the same composition this work is the same for both components.

J. E. T.

Variation of the Specific Heat of Water with the Temperature. *Pernet. Archives de Genève* (*4*) **2**, *531* (*1896*). Previous values determined by Pernet's assistant Lüdin require a slight correction for a more accurate correction of the thermometric readings. It transpires that the mean specific heat of water between 0° and 100° is almost exactly that between 0° and 1°.

J. E. T.

On a New Method of Determining the Densities of Liquids. *R. Zaloziecki. Zeit. angew. Chem.* **1896**, *552*. The author proposes to utilize the fact that when equal volumes of two non-miscible liquids are placed in a calibrated U-tube, the difference in the levels will be proportional to the ratio of the densities. There seems to be nothing to recommend the method. *W. D. B.*

On the Compressibility of Certain Gases at 0° at Ordinary Pressures. *A. Leduc. Comptes rendus*, **123**, *743* (*1896*). The author has determined the variations from the gas law for carbon dioxid, nitrous oxid, hydrochloric acid, ammonia and sulfur dioxid.

W. D. B.

On Certain Abnormal Instances of Solubility. *H. Le Chatelier. Comptes rendus.* **123**, *746* (*1896*). Calcium, barium, magnesium, cadmium and lead sulfates form solid solutions with sodium sulfate as solvent. With magnesium, cadmium and lead sulfates a double sulfate next crystallizes and then the single salt. With barium and calcium sulfates no double sulfates are formed. The sodium magnesium sulfate is stable at its melting point and the same is true for sodium cadmium sulfate. *W. D. B.*

Researches on the Explosive Properties of Acetylene. *M. Berthelot and Vieille. Comptes rendus,* **123,** *523 (1896).* At a pressure of less than two atmospheres there is no explosion wave in acetylene. Neither gaseous nor liquid acetylene will explode under the influence of shock. Liquid acetylene possesses about the same explosive power as gun cotton. The reaction products are carbon and hydrogen; and in one experiment the carbon was changed by the pressure into a lump of coal. *W. D. B.*

Some recent Work on Molecular Physics. *R. A. Fessenden. Jour. Frank. Inst.* **142,** *187 (1896).* The author tries to account for the physical properties of solids by molecular arrangement. To eliminate irregularities he proposes that «the standard physical state of metals be defined as that state which is produced by heating the metals in a vacuum for one hour at a temperature as close to the melting point as possible.» *W. D. B.*

Some Considerations upon the Solubility of Solids in Gases. *H. Arctowski. Zeit. anorg. Chem.* **12,** *413 (1896).* The author is troubled by the fact that the equations of Schröder and of Le Chatelier for saturated solutions can not be applied universally. (One reason for this is that no distinction has been made between solvent and solute). The author proposes to pass continuously from solids in presence of gases to solids in presence of liquids and in this way to eliminate all complications. As a program this is excellent; but this leads at once to a conclusion which the author does not draw, that the vapor pressure of any solid must be changed by the presence of any gas. *W. D. B.*

On Solid Solutions of Phenol and Benzene. *F. Garelli. Gazz. chim. Ital.* **26,** *II, 107 (1896).* Phenol is shown to crystallize with benzene in varying proportions. The method used was that of van Bijlert. *W. D. B.*

Polyvariant Systems

An Attempt to Calculate the Force with which Ether and Chloroform are Attracted to the Nerve Cells in the State of Nar-

cosis. *H. Dreser. Zeit. phys. Chem.* **21**, *108* (*1896*). P. Bert's experiments on the use of anaesthetics have shown that in administering chloroform the most satisfactory results are obtained when the vapors of the anaesthetic are diluted with air in the proportion of 10 grams chloroform to 100 liters air. In this mixture the partial pressure of the chloroform vapor is 14.194 mm at 35°C, the temperature of the air in the lungs.

Dreser regards this pressure as the vapor tension of a solution of chloroform in the blood, in the protoplasm of the nerve cells, *etc.*, and calculates the osmotic pressure that would be set up in a Pfeffer's cell filled with the patient's blood and immersed in pure chloroform at 35°C. He finds 982.4 atm; this is the «force» in question.

For ether, the «optimum» mixture consists of 20 grams ether in 100 liters air, corresponding to a partial pressure of 45.844 mm and an osmotic pressure or force of 703.6 atm.

W. L. M.

The Hydrolysis of Ferric Chlorid. *H. M. Goodwin. Zeit. phys. Chem.* **21**, *1* (*1896*). The author has made a series of measurements at 25°C of the conductivity of ferric chlorid solutions, paying particular attention to the increase in conductivity that accompanies the gradual change of color observed in the more dilute solutions ($FeCl_3$ in 500 liters and over). He explains the gradual increase, by assuming that of the true reactions—electrolytic dissociation, hydrolysis, and polymerization of the ferric hydrate to form Graham's colloid hydrate—the first two, being ion reactions, take place instantaneously on addition of water to the more concentrated solutions, while the third requires more time. The polymerization, by reducing the quantity of ferric hydrate in solution (probably as $FeOH^{\cdot\cdot}$ ions), causes further hydrolysis and a consequent increase in the conductivity due to the hydrochloric acid formed.

From measurement of the conductivity and freezing points the amount of hydrolysis is calculated, and found to vary from almost *nothing* in solution containing $FeCl_3$ in 10 liters, to over 90 per cent when the volume reaches 2000 liters.

If the author's conclusions are to be adopted, a new interpretation must be given to the results of G. Wiedmann's experiments on the magnetism of ferric solutions [*Wied. Ann.* **5**, *45* (*1878*)]; perhaps by ascribing different (specific magnetism) to the various ions and undissociated molecules in the solution. *W. L. M.*

On the Employment of the Boiling-Point Method and on the Influence of Solid Solutes on the Determination of Alcohol. *F. Freyer. Zeit. angew. Chem.* **1896**, *654*. Addition of sugar lowers the boiling point of aqueous alcohol. Sugar and alcohol being non-miscible, the former increases the partial pressure of the latter and this effect happens to be greater than the decrease in the partial pressure of the water.

W. D. B.

On the Viscosity of Mixtures of Liquids. *C. E. Linebarger. Am. Jour. Sci.* (*4*) **2**, *331* (*1896*). The author has determined the change of the viscosity with the concentration for sixteen pairs of normal liquids. In all these cases the values for the solutions lie between those for the pure components. *W. D. B.*

On the Density and Mean Specific Heat between 0° and 100° of Alloys of Iron and Antimony. *J. Laborde. Comptes rendus*, **123**, *227* (*1896*). Some of the alloys are denser than either of the components, the maximum density occurring near the alloy with the composition, Fe_3Sb_4. The specific heats are greater than those calculated from the composition, the maximum variation coinciding with the maximum density. This does not prove the existence of a compound, Fe_3Sb_4, though the author thinks it does.

W. D. B.

Contributions to the Knowledge of Dissociation in Solutions. *W. S. Hendrixson. Zeit. anorg. Chem.* **13**, *73* (*1896*). The distribution of benzoic or salicylic acid between water and benzene or chloroform. After taking into account the electrolytic dissociation in the aqueous phase, the author shows that the polymerization in the other solvent, which must be assumed in order to satisfy the Distribution Law, varies with the concentration according to the Mass Law formula. The results are very satisfactory though it is a question whether with high volume concentrations one can regard the concentration of the solvent as constant. An experiment should have been made to determine the effect of benzoic acid on the mutual solubilities of the two liquids. *W. D. B.*

Osmotic Pressure

The Determination of Isomotic Concentration by Means of the Haematocrit. *S. G. Hedin. Zeit. phys. Chem.* **21**, *272* (*1896*). A criticism of Köppe's paper on the same subject [*Zeit. phys. Chem.* **16**. *261* (*1895*)]. The method in question must be employed with circumspection: many salts (*e. g.*, alkali carbonates and chromates) destroy the blood corpuscles; if the blood used be not defibrinated there is danger of coagulation occcurring during the course of the experiment; the centrifugal apparatus should give a constant, high velocity. *W. L. M.*

Osmotic Pressure. *W. C. D. Whetham. Nature*, **54**, *571* (*1896*). A simple extension of Poynting's ‹theory› (this Journal, **1**, 184) enables the author to retain the view that the ions of dissolved electrolytes are free from one another. «We have only to suppose that, in the case of electrolytes, the dissociated molecules are resolved into their ions, that each ion so produced unites with one solvent molecule, or, at all events, destroys the mobility of one solvent molecule.» Thus «the advantages of the dissociation theory would be retained.» *J. E. T.*

Osmotic Pressure. *J. H. Poynting. Nature*, **55**, *33* (*1896*). Incited by Whetham's article (see foregoing review) Poynting remarks that he means by «dissociation hypothesis» the "dissociation of the atoms in electrolytes from the molecules of solvent.» He agrees with Whetham that the ions may be dissociated «from each other». *J. E. T.*

Velocities

The Dependence of Speed of Diffusion on Initial Concentration in Dilute Solutions. *W. Kawalki. Wied. Ann.* **59**, *637* (*1896*).

Nernst concluded from his discussion of the work of other observers on diffusion that K, the constant of Fick's equation ($\partial u/\partial t = K\partial^2 u/\partial x^2$), becomes nearly or quite constant after a certain dilution has been reached. The present paper describes the results of experiments on aqueous solutions of an electrolyte, NaAc, and a non-electrolyte, carbamid. The two show no striking difference in behavior. The concentration of the salt solution varied in one set of experiments from 3.1 per cent to 0.5 per cent, and that of the carbamid from 4.2 per cent to 0.34 per cent. In each case K showed only irregular variations, and these were larger for the non-electrolyte than for the salt. These variations are explainable by convection currents which have a larger effect as the solutions become more dilute and of more uniform density. The carbamid solutions are lighter than the NaAc solutions which accounts for the greater effect of convection currents. The results as a whole confirm the conclusion of Nernst that at sufficiently great dilutions K is independent of the concentration. They also show that after a certain dilution is reached it becomes impossible to avoid convection currents because of the nearly uniform density of the different liquid layers.

The reviewer would suggest that by carrying on the diffusion in a jelly, convection currents might be entirely avoided.

E. B.

On Autocatalysis. *F. G. Donnan. Ber. chem. Ges. Berlin.* **29,** *2422* (*1896*). From experiments of Goldschmidt [*Ber. chem. Ges. Berlin.* **29,** *2208 ; this Journal,* **1,** *199*] it appears that the etherification of acids by a large excess of alcohol is a *bimolecular* reaction. This Goldschmidt accounts for by assuming that the hydrogen ions of the acid exert a catalytic action on its own etherification ; another explanation is suggested by Donnan as follows :—

If the degree of electrolytic dissociation of the acid be represented by m, then the quantity of undissociated acid remaining at the time t will be $(a - x)(1 - m)$.

From the two equations

$$dx/dt = c(a - x)(1 - m)$$

and

$$k(1 - m) = m^2(a - x)$$

of which the latter is the dissociation isotherms for the acid, V (the volume) and $(a—x)$ being reciprocal quantities, there follows: Donnan's equation

$$dx/dt \quad K'm^2(a-x)^2$$

while Goldschmidt's equation is

$$dx/dt = K'm\,(a-x)^2$$

and for intervals in which m may be regarded as constant the two are identical.

If the reaction be considered to take place between the alcohol and the ions of the acid, Donnan's equation follows at once.

W. L. M.

On the Gradual Oxidation of Hydrogen and of Carbon Monoxid. V. Meyer and Max Recklinghausen. *Ber. chem. Ges. Berlin,* **29**, *2549* (*1896*). Aqueous solutions of potassium permanganate slowly absorb hydrogen and deposit a brown sediment. The authors planned a series of experiments to determine the speed of this reaction, but were diverted from their purpose by the surprising discovery that if the permanganate solution be acidified, the hydrogen absorbed is replaced by about half the volume of *oxygen.* It has long been known that permanganate solutions give off small quantites of oxygen on standing; the authors' experiments show that if shaken with hydrogen the quantity evolved is seven or eight times as great as when air, carbon dioxid or a vacuum is employed. Oxygen stops the evolution of gas; carbon monoxid acts somewhat like hydrogen. A further investigation is promised.

W. L. M.

The Influence of a Pressure of 500 Atmospheres on the Rate of Inversion of Cane Sugar. *O. Stern. Wied. Ann.* **59**, *652* (*1896*). When the inversion was effected by hydrochloric, sulfuric or oxalic acid, increase of pressure reduced the velocity; the greater the concentration of the acid the more noticeable was the effect of pressure. With phosphoric and acetic acids on the other hand the rate of inversion was greater at the high pressure; and the increase in velocity was more considerable when small quantities of acid were employed.

The experiments were carried on at 15°C and at 25°C; the effect of change in pressure is in most cases slightly less at the higher temperature. *Compare V. Rothmund. Zeit. phys. Chem.* **20**, *168 (1896); this Journal* **1**, *123*. *W. L. M.*

On the Rate of the Reaction between Ferric Chlorid and Stannous Chlorid. *A. A. Noyes. Zeit. phys. Chem.* **21**, *16 (1896)*. The author points out that Goodwin's results (this Journal, **1**, 261) tell against Kortright's suggestion that the velocity in question may be modified by hydrolysis of the iron salt. He neglects, however, to state that these results also throw doubt upon the value of his own work in this field.

In his calculations he apparently assumed complete electrolytic dissociation of both the iron and the tin salt, while Goodwin finds the dissociation of Noyes's most concentrated solution about 75% and of his most dilute solution about 50%. If Noyes assumes the speed of reaction the same with the electrolytically dissociated and with the hydrolytically dissociated parts of the ferric chlorid (which seems hardly justified) so that the active mass is the sum of these two substances, he still has about 20% less of the active iron salt than he employs in his calculations. In either case according to the mass law the change of the active mass with the time must vary in a different manner than is given by Noyes's equations.

J. E. T.

Investigations of the Velocity of Sublimation of the Haloid Salts of Mercury. *H. Arctowski. Zeit. anorg. Chem.* **12**, *417 (1896)*. A constant current of air passed over the surface of the salt, and the loss of weight per hour was determined at various temperatures and represented graphically. The order of volatility is mercuric chlorid, mercuric bromid, mercuric iodid and mercurous chlorid. It was found that the salts caked at higher temperatures, and that this had a great effect upon the rate of evaporation. The author does not seem to know that the rates of evaporation for two different substances are necessarily proportional to the vapor pressures only in case the air is completely saturated. *W. D. B.*

Investigations of the Sublimation Pressures of Iodin. *H. Arctowski. Zeit. anorg. Chem.* **12**, *427 (1896)*. The rates of sublima-

tion in an air current of constant velocity were determined for different pressures. By assuming that one rate corresponds to a given pressure, the vapor pressures at other temperatures can be calculated.
W. D. B.

Eletromotive Forces

The Cadmium Normal Cell. *W. Jaeger and R. Wachsmuth. Wied. Ann.* **59**, *575 (1896)*. The Clark cell has an inconveniently large temperature coefficient: $dE/dt = -0.0008$ (volt.degree^{-1}). A similar cell with zinc replaced by cadmium has the advantage of changing its E.M.F. much less with the temperature. The present paper describes the results of research concerning the E.M.F. of the cell, its temperature coefficient, the ease of reproduction and effect of impurities and finally its constancy. The E.M.F. was found by comparison with standard Clarks to be 1.0190 international volts at 20°. The H-form of cell was used and the cadmium was used as a solid amalgam of 6 parts Hg to 1 part Cd. The variation of E.M.F. with the temperature is given by the formula

$$E_t = E_{20} - 3.8 \times 10^{-5} (t - 20) - 0.065 \times 10^{-5} (t - 20)^2$$

between 0° and 26°. The element returns quickly to its normal state after heating. The temparature coefficient at 20° is thus about 1/23d of that of the Clark cell. Directions are given by which the cell may be reproduced so as to give always the same E.M.F. within one ten-thousandth. Ordinary C.P. chemicals from the dealers give values which are the same within a few ten-thousandths. The measurements for constancy extended over two years. The element is as constant as the Clark and sending through the mails leaves the E.M.F. unchanged.
E. B.

Helmholtz's Absolute Electrodynamometer and an Application of it to the Measurement of the Electromotive Force of the Clark Cell. *K. Kahle. Wied. Ann.* **59**, *532 (1896)*. The paper contains a detailed description of the construction of a new form of current balance, together with the measurements and computations needed in using it and a measurement in absolute volts of the E.M.F. of the Clark Cell. This value is the only point in the paper of interest to the physical chemist. The values found were $E_0 = 1.4488$ and $E_{15} = 1.4322$ absolute volts. The cells were of the forms described by the author in *Wied. Ann.* **51**, *203* (*1894*).

E. B.

Hall's Phenomenon in Liquids. *H. Bagard. Jour. de Phys.* (*3*) **5**, 499 (*1896*). The paper described experiments on solutions of $ZnSO_4$ and $CuSO_4$ at various concentrations and at the temperature of the room. The liquid layers were 1 cm thick. The field had the values 385, 707 and 962 C. G. S. The Hall effect is in the same direction as in bismuth. The effect increases with dilution, with current density and with the field. *E. B.*

On the Relation between the Hall Effect and Thermoelectricity in Bismuth and in Various Alloys. *J. C. Beattie. Proc. Roy. Soc. Edinb.* **21**, *146* (*1896*). On arranging metals in the thermoelectric series it appears that those with an extreme position thermoelectrically have a corresponding extreme position as regards the Hall effect, although various «irregularities» appear. The author adds measurements at varying temperatures of the Hall effect with bismuth, and the electromotive force of the thermocouple Bi — Pb, and remarks that we may not yet maintain the transverse effect to be a function of the thermoelectric force. *J. E. T.*

The Depolarization of Platinum and Mercury Electrodes. *G. Meyer and K. Klein. Verh. phys. Ges. Berlin*, **15**, *111* (*1896*). Two electrodes, one 100 to 300 times smaller than the other, were placed in *n*/500 solutions of twelve different electrolytes and the smaller electrode was polarized by currents of slightly over 0.2 volt for times ranging from ten seconds to two minutes. The E.M.F. of polarization was measured by a capillary electrometer of capacity negligible against that of the small electrode. It was found that the size of the relatively small electrode has no influence upon the depolarization, that the velocity of depolarization decreases with increasing time of polarization, that it increases with rising temperature and with solution of a second salt with the acid of the first and the metal of the electrode, that it is the same or less for platinum electrodes than for mercury ones, and that in all cases the anode polarization disappears more rapidly than that at the cathode. These observations are shown to accord with the view that the polarizing E.M.F. changes the concentration at the two electrodes so that the E.M.F. of polarization becomes that of a concentration cell. To calculate the velocity of depolarization the E.M.F. of the concentration cell with the concentration-ratio u_o/u is written

$$x = C\ log_e(u_o/u)$$

and it is assumed that

$$du/dt = \alpha(u_o - u)$$

which is integrated and combined with the former equation and then simplified by introducing for $t = 0$, $x = V$ and $u = u_1$ and writing $b = 1 - e^{-v/c}$,

$$x = V\frac{log_{10}(1 - be^{-\alpha t})}{log_{10}(1 - b)}.$$

This formula represents the results of the authors with a very remarkable exactness. *J. E. T.*

On the Behavior of So-called Unpolarizable Electrodes with Alternating Currents. *E. Warburg. Verh. phys. Ges. Berlin.* **15,** *120 (1896).* In 1872 F. Kohlrausch set the polarization p of an electrode, by an alternating current, proportional to the quantity of electricity which had passed

$$p = \frac{1}{C}\int jdt,$$

j is current, t time and C the ‹capacity for polarization›. One may assume $j = a \sin mt$, but according to recent work of M. Wien and Orlich one must write

$$p = \frac{1}{C}\int a \sin(mt + \psi)dt$$

$$= \frac{a}{Cm}\sin\left[mt - \left(\frac{\pi}{2} - \psi\right)\right]. \qquad \text{(I)}$$

ψ lies somewhere between zero and $\pi/2$. This equation involves p and mt. An expression involving mt and the difference of concentration which is produced, is had by equating the salt transferred from the cathode to the anode with that which would then diffuse in the opposite direction (silver in $AgNO_3$ is supposed); another involving the E.M.F. of polarization and the difference of concentration is given by the Nernst theory, and a combination of both gives a new expression relating p and mt. This, combined with the initial equation (I) yields the values of C and ψ.

The salt transferred electrolytically is

$$\mu = jn(A/107.7)\mathfrak{A},$$

where $\mathfrak{A}$ is its equivalent weight, A the electrochemical equivalent of its cation and n its transference number, and this must equal the amount transferred by diffusion,

$$o = \mu + qk(\partial c/\partial z)_o$$

or

$$\left(\frac{\partial c}{\partial z}\right)_o = -jn\frac{A}{107.7}\frac{\mathfrak{A}}{qk}$$

where q is the cross section of the solution, z the normal distance and k the diffusion constant. At the electrode the alternating current $j = a \sin mt$ produces periodic concentration changes calculable from the diffusion equation

$$\frac{\partial c}{\partial t} = k\frac{\partial^2 c}{\partial z^2}$$

which, integrated under the conditions

1: $z = o$, $\partial c/\partial z = -ba \sin mt$, $b = nA\mathfrak{A}/107.7qk$

2: $z = \infty$, $c = c'$, (*the initial concentration*)

gives for the stationary state, for c when $z = o$,

$$c_o - c' = \frac{ab\zeta}{\sqrt{2}}\cos\left(n + \frac{\pi}{4}\right), \qquad \text{(II)}$$

ζ is the distance from the electrode in which the amplitude of the concentration wave has fallen by $1/e$ of that at the electrode. These waves resemble the temperature waves produced in the earth's crust by the seasons.

From the theory of concentration currents

$$p = R\theta\frac{f}{w}\frac{A}{107.7}n\log\frac{c_o}{c^o}, \qquad \text{(III)}$$

where R, θ, w and f are the gas-constant, absolute temperature, valence and number of ions produced from a molecular weight,—the dissociation is assumed complete. Combining this with (II) and putting the changes of concentration small as against c^o

$$p = R\theta \frac{f}{w} \frac{A}{107.7} n \cdot \frac{ab\zeta}{c^o\sqrt{2}} \sin\left(mt - \frac{\pi}{4}\right). \qquad \text{(IV)}$$

Combining the two relations (I) and (IV) between p and mt gives

$$\frac{C}{q} = 0.00410 \frac{w\sqrt{k}}{n^2 f \mathfrak{A}} \frac{\theta_o c^o}{\theta\sqrt{m}} \quad \text{and} \quad \psi = \frac{\pi}{4}.$$

The author then finds $C/q = 664.8$ *mf* for silver in $AgNO_3$ and calculates some experiments of M. Wien :

$\frac{m}{2\pi}$	$\frac{C}{q}$ in mf.	ψ	$\frac{C}{q}\sqrt{\frac{m}{2\pi}}$
535	538	41°50′	12450
256	842	39	13470
128	1180	42 10	13350
64	1570	45 50	12560

The fourth column is constant, as required by the theory, and ψ is very near $\pi/4 = 45°$. Platinized platinum in NaCl solution agrees approximately, but bright platinum or mercury in solutions of salts of lighter metals do not agree at all with the theory ; the behavior of mercury in sulfuric acid bears upon the theory of the capillary electrometer,—further experimentation is under way.

J. E. T.

Magnetization of Liquids. *J. S. Townsend. Proc. Roy. Soc.* **60**, *189* (*1896*). Measurements of the coefficients of magnetization of solutions of iron salts show this coefficient to be independent of the magnetizing force, at least between 1 and 9 centigram units, and to change with the weight w of iron per cubic centimeter according to the formula

$$10^7 k = 2660\, w - 7.7$$

for ferric salts, and to

$$10^7 k = 2060\, w - 7.7$$

for ferrous salts. The temperature was 10°C. The temperature coefficients are nearly equal at the same temperatures.

J. E. T.

On the Effect of the Röntgen X-rays on the Contact Electricity of Metals. *J. R. Erskine Murray. Proc. Roy. Soc.* **59**, *333* (*1896*). The contact potential difference of plates of zinc and tin foil mounted on ebonite was measured by the Kelvin null method. A value of about + 0.44 volt was changed to — 0.50 when X-rays were turned perpendicularly upon the plates, or from + 0.39 to — 0.39 when they struck in a parallel direction or passed between the plates without striking their surfaces. In each case separating the plates produced but slight deflection of the galvanometer, showing that the rays had decreased the contact potential difference to zero. The author concludes that the rays cause no sudden change in the contact potential, but that the air between them is temporarily converted into an electrolyte whose conduction reduces this potential difference to zero.

J. E. T.

Note on Trithio-dilactic Acid. *J. M. Lovén. Zeit. phys. Chem.* **21**, *134* (*1896*). The silver salt of this acid undergoes spontaneous decomposition within a few minutes of its formation; the author has however succeeded in determining its solubility (approximately) by measuring the E.M.F. of the combination

Ag | Ag salt in *n*/10 sol. of Na-salt | *n*/10 KNO_3 | *n*/10 $AgNO_3$ | Ag.

From the results, 0.157 and 0.171 volt at 15°C, it follows that one gram of the silver salt requires about forty liters of water for solution [Method of calculation, see *Ostwald, Lehrbuch II, 881*].

W. L. M.

Supplement to «Studies on Superoxid Electrodes». *O. F. Tower, Zeit. phys. Chem.* **21**, *90* (*1896*). Owing to an error in certain formulae in a previous paper, [*Zeit. phys. Chem.* **18**, *17* (*1895*)] the values for the H-dissociation of twenty-one salts must be recalculated. The new values are given in tabular form; the results no longer agree with those of Trevor [*Zeit. phys. Chem.* **10**, *32* (*1894*)].

W. L. M.

ON THE LIQUEFACTION OF A MIXTURE OF TWO GASES[1]

BY P. DUHEM

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§ 1. HISTORICAL

In 1880, L. Cailletet made a very important and entirely unexpected observation. Upon compressing a mixture of one volume of air with five volumes of carbon dioxid, in the apparatus employed by him to liquefy the permanent gases, he observed a portion of the mixture assume the liquid state under a moderate pressure; continuing to increase the pressure gradually, that the temperature might remain constant, he saw the liquid disappear when the pressure had attained a certain value[2]. When the pressure was gradually diminished the liquid reappeared suddenly at the moment of reaching the pressure under which it had disappeared in the first experiment; at any given temperature the meniscus was formed as soon as the pressure had attained a definite value, which was the lower the higher the temperature.

The liquid could thus be distinguished from the gas

at 132 atm at the temperature	+ 5.5°C
124	+ 10.
120	+ 13.
113	+ 18.
110	+ 19.

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[1] Translated, by J. E. Trevor, from the author's French manuscript.

[2] L. Cailletet. Expériences sur la compression des mélanges gazeux. Comptes rendus **90**, 210 (1880). Jour. de phys. (1) **9**, 192 (1880).

L. Cailletet et P. Hautefeuille. Recherches sur la liquéfaction des mélanges gazeux. Comptes rendus, **92**, 901 (1881).

and finally at 21° the mixture, even when compressed above 390 atmospheres, was no longer liquefied.

Shortly after Cailletet's communication, and without knowledge of it, van der Waals[1] made an analagous observation. In experimenting with a mixture of nine volumes of carbon dioxid with one volume of air he found, at different temperatures, the following values for the pressure P under which the liquid began to appear, and for the pressure P' under which it disappeared :

at +29.0°C	P	77.5 atm	P'	95 atm
+20.4		72		103
+19.2		72		106
+ 2.0		72		149

A mixture of seven volumes of carbon dioxid with three volumes of hydrochloric acid gave the following results :

at +22.5°C	P	69 atm	P'	115 atm
+ 0.0		39		190

At the temperature 31.6°C the two pressures became equal at 90 atmospheres.

On the 18th of March, 1886, Stokes communicated to the Royal Society of London a posthumous memoir of Andrews.[2] In this memoir the illustrious physicist studied the compressibility of mixtures of nitrogen and carbon dioxid. Three volumes of carbon dioxid when mixed with four volumes of nitrogen could not be liquefied under any pressure, even at the temperature +2°C. On the other hand a mixture of 6.2 volumes of nitrogen with 1 volume of carbon dioxid exhibited the following behavior : At 3.5°C the liquid began to appear under a pressure of 48.3 atmospheres, the quantity of liquid increasing simultaneously with increase of pressure ; under a pressure of 102 atmospheres the gas was reduced to a small bubble, which finally disappeared. At a higher temperature the phenomenon observed by Cailletet and by van der Waals was

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[1] J. D. van der Waals. Die Continuität des gasförmigen und flüssigen Zustandes. Translation by F. Roth, page 143 (Leipzig, 1881).

[2] Andrews. On the Properties of Matter in the Gaseous and Liquid States under Various Conditions of Temperature and Pressure. Phil. Trans. **178**, 57 (1888).

produced; the liquid after having appeared under a certain pressure disappeared under a greater one.

A mixture of 3.43 volumes of carbon dioxid with 1 volume of nitrogen gave the following values for the pressure P under which the liquid appeared and for the pressure P' under which it disappeared:

+6.3°C	P	68.7 atm	P'	113.2 atm
9.9		76.6		107.8
13.2		91.6		103.2

It is seen that the values of P and of P' tend to become equal at 98 atmospheres for a temperature of about 14°.

In 1883 Jamin[1] proposed a theory of the curious phenomenon discovered by Cailletet and by van der Waals. Remarking that the critical point of a single fluid is the point where the gas and the vapor have the same density he supposed that at this temperature the liquid does not cease having properties distinct from those of the vapor, but that having the same specific gravity as the vapor it remains mixed therewith, forming with it a fluid apparently homogeneous. Extending this view to the mixture of two fluids, of air and of carbon dioxid for example, he supposed the disappearance of the liquid mixture under a sufficiently high pressure to be only an apparent disappearance; that the liquid mixture continued to subsist although its density had become equal to that of the gaseous mixture, and that it had diffused into the latter, becoming no longer distinguishable therefrom.

If this theory be true the liquid must disappear under a pressure which is the less the more dense the hardly liquefiable gas which is mixed with the carbon dioxid, and so to make the liquid disappear it would be necessary to employ a much greater pressure when the gaseous component is hydrogen than when it is air; this result foreseen by Jamin was verified by Cailletet. According to Jamin's explanation of the disappearance of the liquid it would seem that in continuing to compress the system the density of the gaseous mixture should become greater than that of the liquid and that in con-

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[1] Jamin. Sur le point critique des gaz liquéfiables. Comptes rendus, 96 (1883); Jour. de phys. (2) **2**, 389 (1883).

sequence the liquid should assemble in the upper part of the tube. Jamin says: «I proposed this second experiment to M. Cailletet, who has made it: the attempt was unsuccessful but I do not yet despair».

The theory of Jamin presents another difficulty not less serious, it is not sufficient that two fluids should have the same density in order that they can form a homogeneous mixture; the experiments of Plateau on the statics of liquids removed from the action of gravity demonstrate this. In order that two fluids initially separated may mix it is necessary that their molecular attractions become the same; at the critical point of a single fluid this condition is evidently satisfied if it be admitted that the liquid and the vapor become identical there; but it is not apparent why two mixtures of carbon dioxid and of air, the one liquid and the other gaseous, should have the same molecular attractions at the moment when they have the same density. Notwithstanding these difficulties of the explanation proposed by Jamin it was still held by Cailletet and Colardeau[1] in 1889.

In 1888 I proposed[2] to abandon Jamin's explanation and to seek to account for the phenomena observed by Cailletet and van der Waals through the theory of double mixtures, as deducible from the principles advanced by J. Willard Gibbs.

Suppose two fluids, 1 and 2, mixed one with the other and forming two layers. The one of these layers is liquid, let it contain a mass M_1 of the body 1 and a mass M_2 of the body 2; the other layer is gas and may contain a mass m_1 of the body 1 and a mass m_2 of the body 2.

Let

$$S = \frac{M_2}{M_1}, \qquad s = \frac{m_2}{m_1}, \qquad (1)$$

be the concentrations of these two layers. Under the constant pressure Π at the temperature T the thermodynamic potential of the first is

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[1] Cailletet and Colardeau. Sur l'état de la matière au voisinage du point critique. Ann. chim. phys. (6) **18**, 269 (1889).

[2] P. Duhem. Sur la liquéfaction de l'acide carbonique au présence de l'air. Jour. de phys. (2) **7**, 198 (1888).

$$M_1 F_1(S,\Pi,T)+M_2 F_2(S,\Pi,T),$$

the thermodynamic potential of the second is

$$m_1 f_1(s,\Pi,T)+m_2 f_2(s,\Pi,T),$$

and the system is in equilibrium when

$$\begin{aligned} f_1(s,\Pi,T) &= F_1(S,\Pi,T), \\ f_2(s,\Pi,T) &= F_2(S,\Pi,T). \end{aligned} \qquad (2)$$

If we assign the values of

$$\begin{aligned} \mathfrak{M}_1 &= m_1+M_1, \\ \mathfrak{M}_2 &= m_2+M_2, \end{aligned}$$

the equations (1) and (2) will yield for each pressure Π and each temperature T the values of m_1, M_1, m_2, M_2.

If we set

$$X = \frac{\mathfrak{M}_2}{\mathfrak{M}_1},$$

we shall obviously find

$$M_1 = G(X,\Pi,T)\mathfrak{M}_1.$$

If $G(X, \Pi, T)$ is positive, this equation will make known the mass M_1 of the fluid 1 which is in the liquid state; if $G(X, \Pi, T)$ is negative, the equation constitutes an impossibility and the gaseous mixture will remain homogenous. Between these two general cases appears the particular case where

$$G(X,\Pi,T) = 0. \qquad (3)$$

This equation defines, for a gaseous mixture of the concentration X at the temperature T, the pressure Π under which the mixture will be in equilibrium with an indefinitely small drop of the liquid. Or, if preferred, it defines the *dew point* T of the gaseous mixture having the composition X under the pressure Π; whence the name of the *dew line* of the mixture of the concentration X, given by me in a previous memoir[1] to the line represented by equation (3) when X is regarded as a constant, T as an abscissa and Π as an ordinate.

To account for the curious fact demonstrated first by Cailletet

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[1] P. Duhem. Dissolutions et mélanges. Troisième Mémoire : Les mélanges doubles. Travaux et mémoires des Facultés de Lille, 3, No. 13 (1893).

and later by van der Waals it is sufficient to admit that for certain concentrations X of the gaseous mixture the dew line presents two ordinates Π_0 and Π_1 for a same abscissa T; when compressed at the constant temperature T the gaseous mixture will remain homogeneous under pressures less than Π_0; under the pressure Π_0 the liquid will appear, the system will contain gas and liquid together between the pressures Π_0 and Π_1; and finally under the pressure Π_1 the liquid will disappear not to appear again under any pressure. When the temperature T rises towards a certain temperature ϑ the two pressures Π_0 and Π_1 tend towards a common limit π, in such wise that the dew line has a form similar to that represented by Fig. 1.

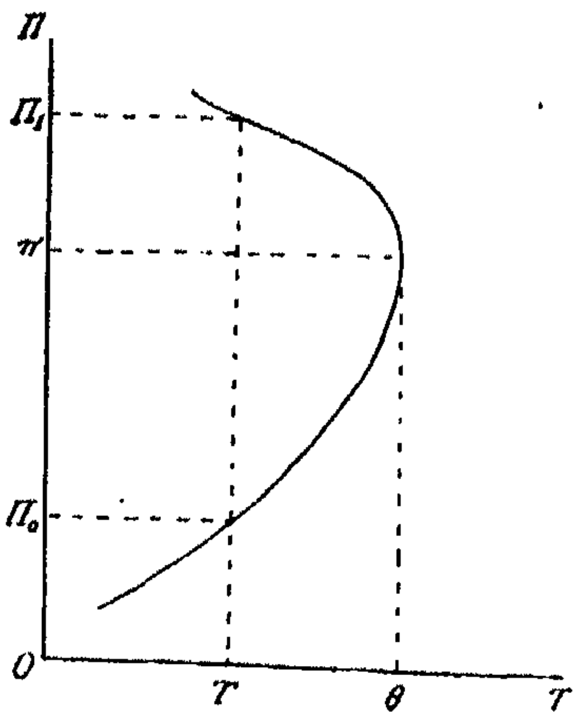

Fig. 1.

My paper was already printed when there appeared in the Philosophical Transactions of the Royal Society of London a posthumous memoir by Andrews[1], which Stokes had presented to this Society on the 18th of March, 1886. In this memoir the illustrious discoverer of the critical point studies the compressibility of a mixture of nitrogen and of carbon dioxid, finding again the phenomenon discovered by Cailletet.

A mixture of 3.43 volumes of carbon dioxid with one volume of nitrogen gave the following values for the pressure Π_0 under which the liquid appeared and for the pressure Π_1 under which it disappeared:

+0.3°C	Π_0 = 68.7 atm	Π_1 = 113.2 atm
9.9	76.6	107.8
13.2	91.6	103.2

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[1] Andrews. On the properties of matter in the gaseous and liquid states under various conditions of temperature and pressure. Phil. Trans. **178**, 37 (1888).

It is seen that the values Π_0 and Π_1 tend to become equal, and equal to 98 atmospheres for a temperature of about +14°C, in conformity with the indications of my theoretical ideas.

It results clearly from the formulas given by me in 1888 that, in the system compressed at the constant temperature T, the liquid mass passes from zero at the pressure Π_0 to return to zero when the pressure again assumes the value Π_1; and that, consequently, in the interval the liquid mass increases, passes through a maximum, and then decreases. These propositions are such obvious consequences of my formulas that I did not think it necessary to state them explicitly. I did not suppose it could be doubted that they result from my view, yet this doubt has been raised, so it must be considered. In the observations of Cailletet, of van der Waals and of Andrews the liquid mass did not approach disappearance by decreasing to zero amount, the surface separating the liquid and the gas became simply plane and indistinct when the pressure approached Π_1; it then disappeared and the two seemed homogeneous.

In comparing the results of my theory with the observations of the experimenters cited I drew attention only to the general accordance between them, without seriously considering this partial lack of agreement, for it did not seem to me at all improbable that Cailletet, van der Waals and Andrews had not really observed states of equilibrium. In these phenomena, as in the vaporization of a liquid near its critical point, the *viscosity*, negligible under other circumstances, assumes a considerable importance; the equilibrium is established with an extraordinary slowness, from which must follow apparent contradictions between the results of rapidly made experiments and the consequences of a theory treating only systems in equilibrium.

P. Kuenen[1] has concluded from my failure to draw attention to this divergence in my memoir of 1888 that I did not at that time admit the existence, between the pressures Π_0 and Π_1, of a progressive condensation causing the mass of the liquid to increase continuously from zero *and followed by a retrograde condensation decreas-*

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[1] Kuenen. On the condensation of a mixture of two gases. Communications from the laboratory of physics at the University of Leiden. No. 13 (1894).

ing this mass continuously to zero. To sustain this opinion would be to maintain that I did not understand the formulas which I advanced nor the reasoning through which they were established. Kuenen could argue from my silence concerning this apparent experimental contradiction to accuse me of temerity; but he himself has brought me justification, for in taking care to agitate the gaseous mixtures studied, in order to assure the prompt establishment of states of equilibrium, he has observed[1] the appearance of the retrograde condensation which stood already written in my formulas.

The object of Kuenen's first paper was to supply experimental data for an important theory developed by van der Waals[2]. If the concentration of the mixture be denoted by s, its density by ρ, and its absolute temperature by T, the inner themodynamic potential of its unit of mass can be represented by $Z(\rho, s, T)$. It has two different values, depending upon whether the mixture is in the liquid state or in that of gas; van der Waals admits that these two values are two different determinations of the same multiform analytic function. He then introduces the following change of variables:

$$\rho = \frac{1}{v}, \qquad s = \frac{x}{1-x},$$

which transforms the function $Z(\rho, s, T)$ into a function $\psi(x, v, T)$. Leaving then the temperature T constant and representing in three rectangular axes the values of the variables x, v and ψ, he proposes to construct the surface

$$\psi = \psi(x, v, T).$$

With this surface constructed, the properties of the mixture, its homogeneous constitution or its separation into two layers, can be studied by the methods which Gibbs has applied to the surface representing the inner thermodynamic potential of a single fluid as a function of its specific volume and of its temperature.

In order to determine the form of the surface ψ, van der Waals is obliged to introduce numerous hypotheses. In the first place he

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[1] Kuenen. Mésures concernant la surface de van der Waals pour des mélanges d'acide carbonique et de chlorure de methyle. Arch. néerl. **26**, 394 (1892).

[2] van der Waals. Théorie moléculaire d'une substance composée de deux matières différentes. Ibid, **24**, 1 (1891).

supposes that the specific volume v, the pressure Π and the temperature T are united through a relation of the form

$$\Pi=\frac{RT}{v-b}-\frac{a}{v^2},$$

previously proposed by him for a single fluid; but here a and b, instead of being constants, are functions of x, he assigns to them expressions of the following form:

$$\left\{\begin{array}{l} a=a_1(1-x)^2+2a_{12}x(1-x)+a_2x^2, \\ b=b_1(1-x)^2+2b_{12}x(1-x)+b_2x^2, \end{array}\right. \tag{4}$$

where a_1, a_{12}, a_2, b_1, b_{12}, b_2 are six constants.

The expression of Π as a function of v, x and T can serve through aid of the well known equation

$$\frac{\partial}{\partial v}\psi(x,v,T)+\Pi=0,$$

for the determination of $\psi\ (x,\ v,\ T)$, nevertheless it determines this function $\psi\ (x,\ v,\ T)$ only *with a function of the variables x and T left arbitrary.* Through a series of considerations, whose precision leaves something to be desired, van der Waals succeeds in *suppressing this function*, whereby ψ is reduced to the form

$$\psi=-\log(v-b)-\frac{a}{v}+RT[x\log x+(1-x)\log(1-x)] \tag{5}$$

where a and b have the values (4). He admits finally that one must have, for the stability of the mixture, the inequality

$$\frac{\partial^2\psi}{\partial x^2}\frac{\partial^2\psi}{\partial v^2}-\left(\frac{\partial^2\psi}{\partial x\partial v}\right)^2>0$$

but this inequality, taken from Gibbs, has not been established in a satisfactory manner, as I have elsewhere remarked[1].

Notwithstanding the employment of all these hypotheses van der Waals cannot *deduce* from the equation of the surface ψ the necessity of the curious phenomenon observed by Cailletet and himself[2], he shows only that it is possible to conceive a mode of variation

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[1] P. Duhem. Dissolutions et mélanges. Premier Mémoire: Equilibres et mouvement des fluides mélangés. Travaux et Mémoires des Facultés de Lille. No. 11, 90 (1892).

[2] van der Waals. *l. c.* 54.

of this surface with the temperature which accords with that observation ; in the paper of van der Waals, therefore, as in that published by me three years before, the retrograde condensation is regarded not as a consequence of the theory but as a result which the theory must be made to represent.

The University of Leyden having set for competition the following question : « Required observations serving to check the theory of van der Waals concerning mixtures of two substances », Kuenen presented a paper which was awarded the prize[1]. In this work Kuenen analyzes the mode of variation of the fold devised by van der Waals to make the general form of the surface ψ conform with the phenomenon of retrograde condensation. He shows that the form of the dew curve must be that represented by Fig. 2. This curve rises from left to right to the point $M(\vartheta,\pi)$; it then rises further, from right to left, up to the point $Z(\Theta,\mathfrak{P})$ where it terminates. At temperatures above ϑ no condensation is possible ; at temperatures below Θ only normal condensation can appear, and finally, at temperatures between ϑ and Θ a normal condensation followed by retrograde condensation is observed.

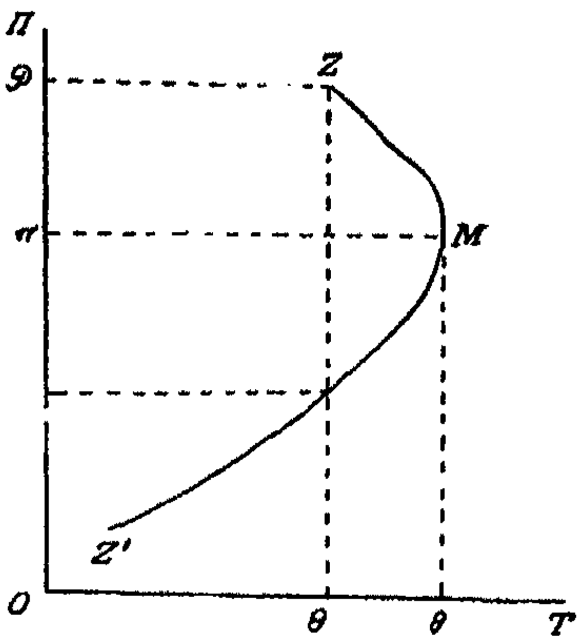

FIG. 2.

The point $M(\vartheta,\pi)$, which had already figured in my exposition, received from Kuenen the name of *point of critical contact ;* the point $Z(\Theta,\mathfrak{P})$, which I had not considered at all, is called the *point of folding*. These terms are chosen because of the parts played by these points in the surface of van der Waals. Kuenen made definite

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[1] P. Kuenen. Metingen betreffende het opperolak van van der Waals voor mengsels van Koolzuur en chlormethyl. Proefschrift. Leiden (1892). Measurements relating to the surface of van der Waals for mixtures of carbonic acid and methyl chloride. Arch. néerl. **26** (1892).

the idea of the point of folding by remarking[1] that *in this point the liquid mixture and the gaseous mixture become identical.*

One is led in fact, by generalization of the theories relative to the continuity of the liquid and gaseous states, to conclude that the two functions $f_1(s, \Pi, T)$ and $F_1(s, \Pi, T)$ are two branches of the same multiform analytic function; and that this is also true of the functions $f_2(s, \Pi, T)$ and $F_2(s, \Pi, T)$. In every point $(\mathfrak{S}, \mathfrak{T}, \Theta)$ of a given *critical line*, the two functions f_1 and F_1 unite and are then prolonged in a single function; the two functions f_2 and F_2 unite likewise to be prolonged in a single analytic function. In the (T, Π)-plane the critical line of the space is projected as a plane critical line uniting the critical point C_1 of the pure fluid 1, $(s=0)$, with the critical point C_2 of the pure fluid 2, $(s=\infty)$. I developed[2] in 1893 this notion of the critical line and proposed, as a consequence, to give the name *critical point*, of the gaseous mixture of the composition X, to the point $Z(\mathfrak{T}, \Theta)$ where the dew curve of this mixture terminates,—to the point termed by Kuenen the *point of folding*.

How, now, does the dew line vary when the concentration X of the gaseous mixture varies from zero to infinity? I have supposed that, for every concentration X_1, X_2, sufficiently near zero or infinity, the dew curve rises continuously from left to right as do the curves $X_1X'_1$, $X_2X'_2$, of the figure 3; for such a concentration the retrograde condensation could not appear. This phenomenon would appear only for the concentrations Z comprised between a lower limit Y_1 and an upper limit Y_2; to such a concentration would correspond a dew curve like ZZ'. To the two limiting concentrations Y_1 and Y_2 there would

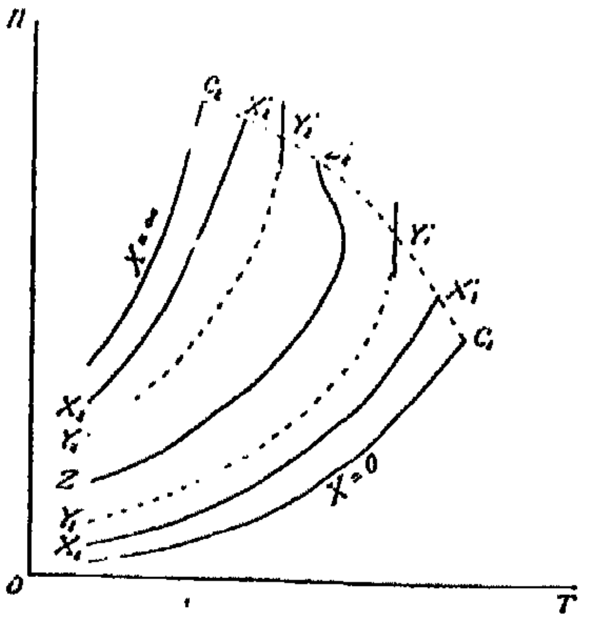

FIG. 3.

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[1] Kuenen, *l. c.* No. 42.

[2] P. Duhem. Dissolutions et mélanges. Troisième Mémoire : Les mélanges doubles. Chap. 2 and 3. Travaux et Mémoires des Facultés de Lille. No. 13.

correspond dew curves $Y_1Y'_1$, $Y_2Y'_2$, which would cut the critical line in points Y'_1, Y'_2 where they would have vertical tangents.

Kuenen[1] has shown that this shape of the dew curves is not in conformity with the geometric theory of van der Waals; that whatever the composition X of the gaseous mixture, the dew curve has the shape which is assigned in Fig. 3 to the line ZZ', such that for every composition of this mixture the retrograde condensation is observable. He has sought to demonstrate, further, that this view follows from the principles posited by me; to supply this demonstration he has proceeded much as follows:—

He remarks very justly at the outset that to the *dew curve* of the *gaseous* mixture having the concentration X—*i. e.*, the curve indicating at each temperature T the pressure Π under which the mixture ceases to be homogeneous or commences to be so—one must join the *boiling curve* of the *liquid* mixture of the concentration X, *i. e.*, the curve which indicates under what pressure Π at each temperature T the liquid homogeneous mixture of the concentration X can be in equilibrium with an indefinitely small gaseous bubble.

The equation of the boiling line is then obtained by the procedure which yields the equation of the dew line; it suffices to permute the functions f_1 and F_1 as well as the functions f_2 and F_2. If it be recollected that the functions f_1 and F_1 are but two distinct determinations of two multiform analytic functions, and that the same is true of the two functions f_2 and F_2, it is seen that the dew line of a gaseous mixture having the concentration X and the boiling line of a liquid mixture of the same concentration X are but two different branches of the same curve, and it is seen further that these two branches must meet at the same point of the critical line C_1C_2. Kuenen has succeeded in deducing from my formulas that the dew line and the boiling line must have the same tangent at this critical point.

Do these two lines meet at the critical point so as to form a single analytic line, or are they mutually tangent in such wise as together to form a curve whose critical point is a cusp? Both hypotheses are admissible.

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[1] Kuenen. On the Condensation of a Mixture of two Gases. Communications from the Laboratory of Physics at the University of Leiden. No. 13 (1894).

Of these two hypotheses Kuenen adopts the first. The critical line C_1C_2 is then, as can easily be shown, tangent to the two lines, the dew curve and the boiling curve, at the point where the latter meet. The dew line XY and the boiling line ZY form thus a curve as represented by Fig. 4.

In the region XYC_1, the mixture in equilibrium is in the state of homogeneous vapor, in the region situated beyond the critical line C_1C_2 it is in the state of homogeneous gas, in the region C_2YZ it is in the state of homogeneous liquid, and in the region XYZ, finally, it is partly in the state of vapor, partly in that of liquid.

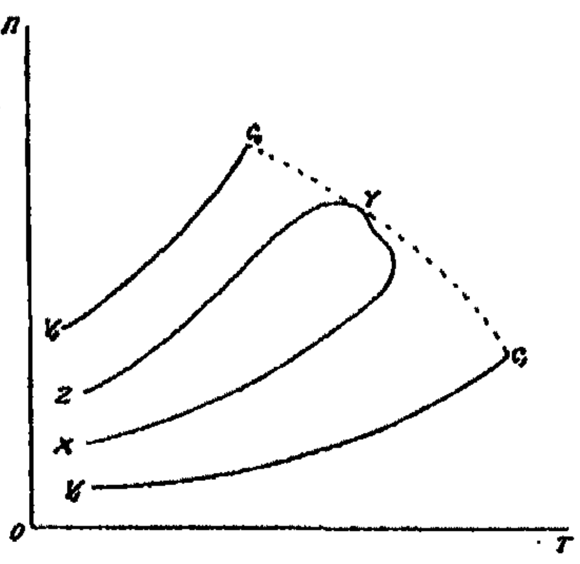

Fig. 4.

When the concentration X tends toward zero or towards infinity the two branches of the curve, XY, ZY, tend towards each other in such wise as to approach either the curve V_1C_1 of the vapor pressures of the liquid 1, or the curve V_2C_2 of the vapor pressures of the liquid 2; each of these curves must be considered in the actual problem as a *double line*, playing at the same time the parts of dew line and of boiling line. One of the two lines, ZY, XY, must, in a part of its extent, be met twice by a same ordinate; Kuenen admits that this property belongs always to the line XY, now if this were true *the phenomenon of retrograde condensation could be observed foı every concentration of the gaseous mixture between zero and infinity.*

This conclusion of Kuenen is seen to rest upon two assumptions which are not above objection, for the recent experiments made by this physicist[1] on the liquefaction of mixtures of ethane and of peroxid of nitrogen relate to a case where the dew line and the boiling line lie too close together for it to be possible to draw from the exper-

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[1] Kuenen. On the Condensation and the Critical Phenomena of Mixtures of Ethane and Nitrous Oxide. Communications from the Laboratory of Physics of the University of Leiden. No. 16 (1895). Phil. Mag. [5] 40, 173 (1895).

iments any very positive conclusion either for or against the existence of a cusp at the junction of the two. Now, if the dew line and the boiling line do meet to form a cusp, my hypothesis concerning the form of the dew lines would be perfectly admissible.

It has therefore seemed to me to be worth while to investigate whether the general theorems which I have established concerning double mixtures will not furnish a means of elucidating the contested points of this problem; the results which I have reached, and which are set forth in the present paper, confirm Kuenen's view—much to my gratification.

§ 2. CONDENSATION AND RETROGRADE CONDENSATION

Let us consider the critical line of a mixture of two bodies 1 and 2; this line connects the critical point $C_1(\mathfrak{P}_1, \Theta_1)$ of the fluid 1 with the critical point $C_2(\mathfrak{P}_2, \Theta_2)$ of the fluid 2.

We shall suppose, in the first place, that, whatever be the concentration of the mixture, its critical pressure will lie between the critical pressures, $\mathfrak{P}_1$ and $\mathfrak{P}_2$ of the fluids 1 and 2.

There is nothing necessary in this hypothesis, but it holds good in every case which has been experimentally studied. If a mixture should be found whose behavior does not accord with it, the following reasoning must, for that mixture, be replaced by analogous but more complicated expressions.

We shall not make an analogous hypothesis concerning the critical temperatures of mixtures, experiment in fact, supplies mixtures whose critical temperatures lie below the critical temperatures of the component fluids; such is, according to Dewar[1], a mixture of CO_2 and C_2H_2 and, according to Kuenen[2], a mixture of NO_2 and C_2H_6.

The hypothesis just formulated is contained, at least in so far as all particular consequences are concerned, in the following hypothesis, which likewise is true for all mixtures yet experimentally studied, and which is taken as the point of departure of the reasoning to be adduced:

There exists one and only one mixture of the two fluids 1 and 2

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[1] Proc. Roy. Soc. 30, 543.

[2] Communications from the Laboratory of Leiden. No. 16, page 21.

having for its critical pressure a certain pressure $\mathfrak{P}$ lying between $\mathfrak{P}_1$ and $\mathfrak{P}_2$.

We designate the concentration of this mixture by $\mathfrak{X}(\mathfrak{P})$ and its critical temperature by $\Theta(\mathfrak{P})$; $\mathfrak{X}(\mathfrak{P})$ and $\Theta(\mathfrak{P})$ are, according to the foregoing hypothesis, uniform functions of $\mathfrak{P}$.

There exists an analytic function, continuous but multiform, of the three variables x, Π, T,—say $\psi_1(x, \Pi, T)$—which coincides, according to the case, either with the function $f_1(x, \Pi, T)$ or with the function $F_1(x, \Pi, T)$. Let us select a constant pressure $\mathfrak{P}$, lying between $\mathfrak{P}_1$ and $\mathfrak{P}_2$, and examine the manner in which the function $\psi_1(x, \mathfrak{P}, T)$ varies with the concentration x and the temperature T.

At temperatures T, above $\Theta(\mathfrak{P})$, the mixture of the concentration x is homogeneous, whatever value x may have; if the pressure $\mathfrak{P}$ and the temperature T are maintained constant, the function $y = \psi_1(x, \mathfrak{P}, T)$ is a constantly and continuously decreasing function of x, represented, from $x = 0$ to $x = +\infty$, by an analytic curve such as $\Phi_1\varphi_1$ (Fig. 5).

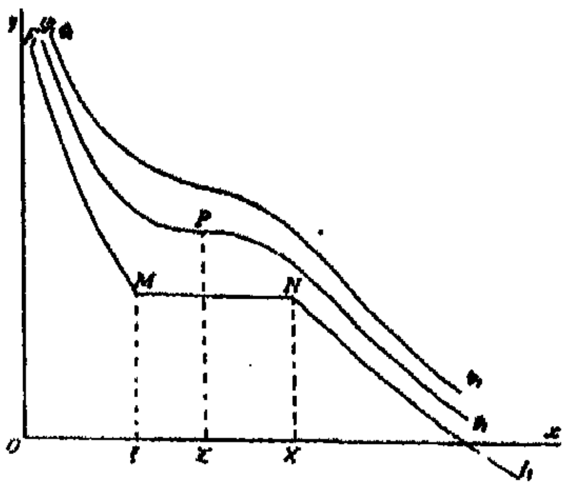

FIG. 5.

At temperatures below $\Theta(\mathfrak{P})$ it can happen that the mixture having the gross concentration x separates into two layers, the one liquid the other gaseous, of different concentrations; for an assigned value T of the temperature, the pressure $\mathfrak{P}$ remaining fixed, the concentration ξ of the liquid layer and the concentration X of the gaseous layer have determinate values.

In certain cases the two preceding propositions must be replaced by those obtained through interchanging the words: *temperatures above $\Theta(\mathfrak{P})$, and temperatures below $\Theta(\mathfrak{P})$*. We shall commence by studying the case just defined, which shall be termed the First Case; we shall then pass to the inverse or Second Case.

Suppose, to fix our ideas, that

$$\mathfrak{P}_2 > \mathfrak{P}_1$$

we admit then that continually

$$X > \xi.$$

When X varies from 0 to ξ. the function $\psi_1(x, \mathfrak{P}, T)$ coincides with the function $F_1(x, \mathfrak{P}, T)$; when x varies from X to $+\infty$, the function $\psi_1(x, \mathfrak{P}, T)$ coincides with the function $f_1(x, \mathfrak{P}, T)$. If it be observed that

$$f_1(X, \mathfrak{P}, T) = F_1(\xi, \mathfrak{P}, T),$$

it is seen that the first branch of the function is represented by the descending curve $F_1 M$ (Fig. 5) and that its second branch is represented by the descending curve Nf_1, the two points M, with the abscissa ξ_1 and N with the abscissa X, have the same ordinate.

Finally, if the temperature T is equal to $\Theta(\mathfrak{P})$, the curve represented by the equation

$$y = \psi_1(x, \mathfrak{P}, \Theta)$$

is a curve $\Psi_1 \psi_1$ (Fig. 5), which falls continuously from left to right, save at the point P, with the abscissa $\mathfrak{X}(\mathfrak{P})$, where it presents a point of inflection with a horizontal tangent.

Thus, *under the given pressure* $\mathfrak{P}$, at each temperature T, there is an entirely determinate curve

$$y = \Psi_1(x, \mathfrak{P}, T),$$

which may be termed the Isotherm relative to the temperature T.

If for the curve

$$y = \Psi_1(x, \mathfrak{P}, T),$$

there be substituted that represented by the equation

$$y = \Psi_1(x, \mathfrak{P}, T) + G(T),$$

where $G(T)$ is an arbitrary function of the temperature T, there is obtained a new curve which is deduced from the first by displacement of all its points, in the direction parallel to Oy, through the same distance $G(T)$. One can evidently make disposition of the function $G(T)$ in such manner that the isotherms which correspond to any two different temperatures may have no common point at a finite distance, and that to the temperatures T, T', T'', . . . all lying below $\Theta(\mathfrak{P})$ and arranged in order of increasing magnitude, there correspond straight lines $MN, M'N', M''N''$, . . . whose ordinates are also arranged in the order of increasing magnitude (Fig. 6). Such a disposition greatly facilitates the discussion, it shall be supposed in the following to be always realized.

The curve which is the locus of the points M, M', M'', . . . and that which is the locus of the points N, N', N'', . . . terminate at the point P; from analogy with the teachings of the theory of the continuity of the liquid and gaseous states, regarding the isotherms of a single fluid, we are led to admit the following hypothesis—upon which this entire discussion rests:

HYPOTHESIS.—*The curve which is the locus of the points M, M', M'', . . . and that which is the locus of the points N, N', N'', . . . have in P a common tangent parallel to Ox,—they extend each other.*

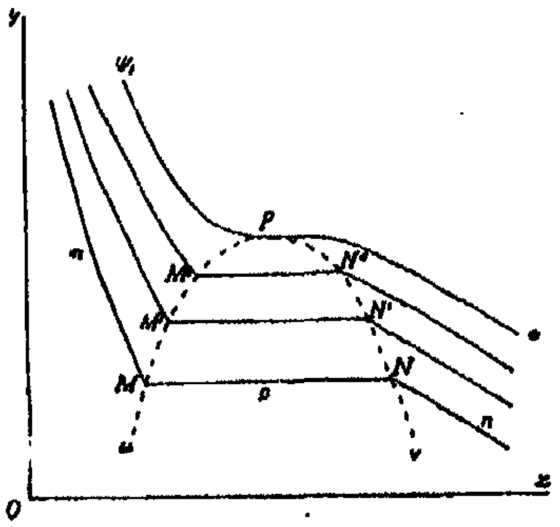

FIG. 6.

The line $\mu P \nu$ formed by these two curves (Fig. 6) possesses remarkable properties.

1st. Take a point m, whose abscissa is x, *in the region* $\Psi_{,} P \mu$. Through this point there passes a line

$$y = \Psi_{,}(x, \mathfrak{P}, T),$$

corresponding to a certain temperature T; *under the pressure* $\mathfrak{P}$, *at the temperature* T, *the mixture having the total concentration* x *is in the homogeneous liquid state.*

2d. Take a point n, whose abscissa is x, *in the region* $\nu P \psi_{,}$. Through this point there passes a line

$$y = \psi_{,}(x, \mathfrak{P}, T),$$

corresponding to a certain temperature T; *under the pressure* $\mathfrak{P}$, *at the temperature* T, *the mixture with the total concentration* x *is in the homogeneous gaseous state.*

3d. Take finally a point p, whose abscissa is x, *in the interior region of the curve* $\mu P \nu$. Through this point draw a parallel to Ox; this line will meet the curve $\mu P \nu$ in two points M, N, where terminate two branches of the same curve

$$y = \psi_{,}(x, \mathfrak{P}, T),$$

corresponding to a certain temperature T. This curve corresponds to a certain temperature T. *Under the pressure* $\mathfrak{P}$, *at the temperature* T, *the mixture of the total concentration* x *is partly in the liquid state and partly in that of vapor.*

The foregoing propositions can be enunciated briefly in the statement that, *under the pressure* $\mathfrak{P}$,

1st. *Every point of the region* $\Psi_, P\mu$ *represents a homogeneous liquid state;*

2d. *Every point of the region* $\Psi_, P\nu$ *represents a state of homogeneous vapor;*

3d. *Every point of the region* $\mu P\nu$ *represents a heterogeneous state.*

Let us consider the part of the curve $\mu P\nu$ (Fig. 7) in the neighborhood of the point P, whose abscissa is $\mathfrak{X}(\mathfrak{P})$.

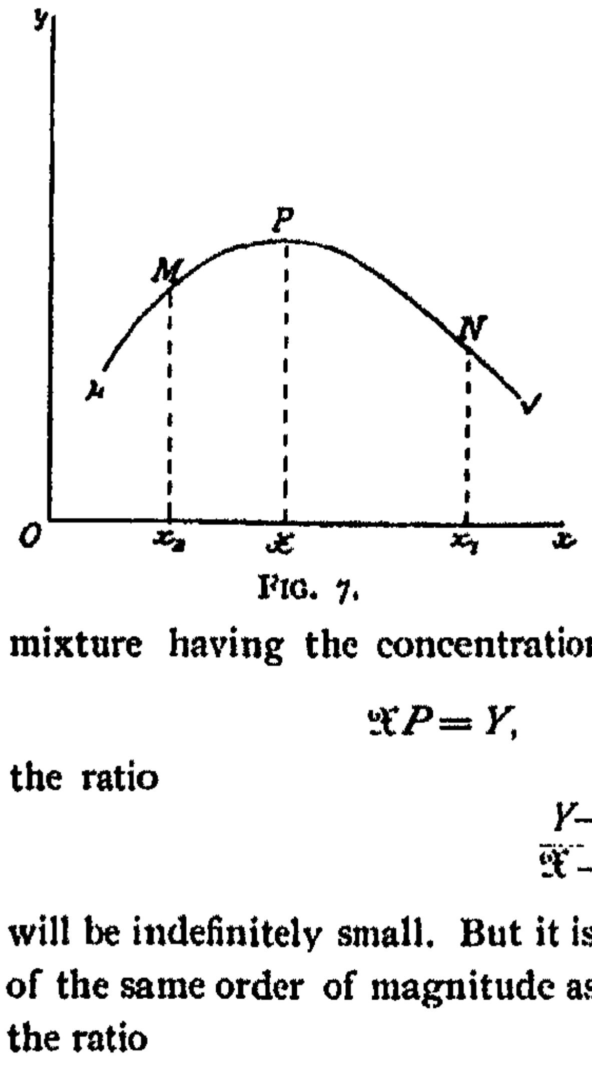

FIG. 7.

We will take a value $x_,$ of x, in the neighborhood of $\mathfrak{X}(\mathfrak{P})$ and above it, from the abscissa $x_,$ we will draw a parallel to Oy; this parallel meets the curve $\mu P\nu$ at a point N, which belongs to the isotherm for a certain temperature $T_,$, lower than $\Theta(\mathfrak{P})$. According to the preceding theorems, $T_, < \Theta(\mathfrak{P})$ and $\mathfrak{P}$ will be the abscissa and the ordinate of a point of the dew line of the mixture having the concentration $x_, > \mathfrak{X}(\mathfrak{P})$. Further, if we set

$$\mathfrak{X}P = Y, \qquad x_, N = y_,,$$

the ratio

$$\frac{Y - y_,}{\mathfrak{X} - x_,}$$

will be indefinitely small. But it is clear that $(Y - y_,)$ is, in general, of the same order of magnitude as $[\Theta(\mathfrak{P}) - T_,]$, in such wise that the ratio

$$\frac{\Theta(\mathfrak{P}) - T_,}{\mathfrak{X}(\mathfrak{P}) - x_,}$$

will be indefinitely small.

We will take, next, a value x_2 of x, near to $\mathfrak{X}(\mathfrak{P})$, and less than $\mathfrak{X}(\mathfrak{P})$; at the abscissa x_2 we will draw a parallel to Oy; this parallel meets the curve $\mu P \nu$ in a point M belonging to the isotherm for a certain temperature T_2 lower than $\Theta(\mathfrak{P})$. According to the preceding theorems, $T_2 < \Theta(\mathfrak{P})$ and $\mathfrak{P}$ will be the abscissa and ordinate of a point of the boiling line of the mixture having the concentration $x_2 < \mathfrak{X}(\mathfrak{P})$. One readily sees, further, that the ratio

$$\frac{\Theta(\mathfrak{P})-T_2}{\mathfrak{X}(\mathfrak{P})-x_2}$$

is indefinitely small. It will be seen that these theorems involve the correctness of the propositions under discussion.

Let us take (Fig. 8) the temperature axis as axis of abscissas and the pressure axis as that of ordinates; let $C(\Theta,\mathfrak{P})$ be a point of the critical line, corresponding to the value $\mathfrak{X}$ of the concentration. From the point C, we will draw a parallel $\mathfrak{P}C$ to the temperature axis. That part of this line $\mathfrak{P}C$ lying beyond the point C meets, in the neighborhood of the point C, neither the dew line nor the boiling line for a mixture whose concentration lies near $\mathfrak{X}$. On the contrary, from every point M, near to the point C on the line $\mathfrak{P}C$ and lying to the left of the point C, there passes a dew line for a mixture of the concentration x_1, greater than $\mathfrak{X}$ and very near it; and a boiling line for a mixture $\mathfrak{X}$ of the concentration x_2, less than $\mathfrak{X}$ and very near it; furthermore the two ratios

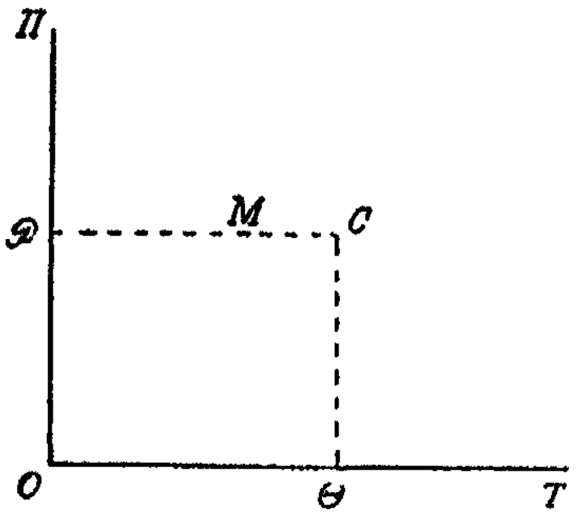

FIG. 8.

$$\frac{\overline{MC}}{x_1-\mathfrak{X}}, \quad \frac{\overline{MC}}{x_2-\mathfrak{X}}$$

tend towards zero when the point M tends towards the point C.

Without further extending this demonstration it may be remarked that to every value $\mathfrak{X}$ of the concentration there corresponds one and but one point C of the critical line, and the reverse;

when $\mathfrak{X}$ varies continuously from zero to unity the point C traverses the critical line from the point C_1, the critical point of the pure fluid 1, to the point C_2, the critical point of the pure fluid 2. If C, C', be two points lying near the critical line, corresponding to the values $\mathfrak{X}, \mathfrak{X}'$, of the concentration; the ratio $\frac{\mathfrak{X}'-\mathfrak{X}}{CC'}$ will tend, in general, towards a finite limit when the two points C, C' tend to come together.

On the other hand we have supposed that

$$\mathfrak{P}_2 > \mathfrak{P}_1$$

and also that there exists one and but one mixture having for its critical pressure some pressure $\mathfrak{P}$ lying between $\mathfrak{P}_1$ and $\mathfrak{P}_2$; it results from this, as is readily seen, that if the concentration of the mixture rises continuously from zero to one, the critical pressure increases continuously from $\mathfrak{P}_1$ to $\mathfrak{P}_2$.

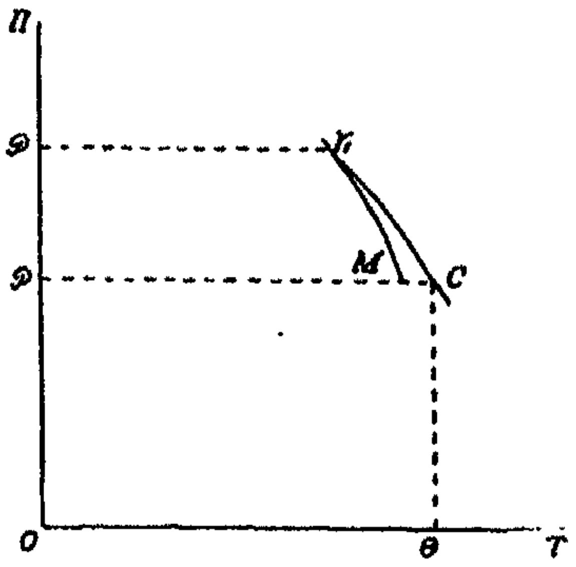

FIG. 9.

These preliminaries settled let us consider a pressure $\mathfrak{P}$ lying between $\mathfrak{P}_1$ and $\mathfrak{P}_2$; the constant ordinate $\mathfrak{P}$ parallel to OT (Fig. 9) meets the critical line in one and but one point C, which is the critical point of a mixture having the concentration $\mathfrak{X}$.

Let us take a point M indefinitely near the point C and lying to the right of it. Through this point passes the dew line of the mixture with the concentration x_1, indefinitely near to $\mathfrak{X}_1$, and greater than $\mathfrak{X}$.

After what has just been shown, the mixture with the concentration x_1 will have as critical point a point γ_1, with an ordinate $\mathfrak{P}_1$ greater than $\mathfrak{P}$. The line $\gamma_1 C$ will be an element of the critical line, and the line $\gamma_1 M$ an element of the dew line, of the mixture having a concentration x_1.

The ratio $\frac{\overline{MC}}{x_1-\mathfrak{X}}$ is infinitesimal; and, on the other hand, it has been shown that the ratio $\frac{x_{,}-\mathfrak{X}}{y_{,}C}$ is finite; but the ratio $\frac{MC}{y_{,}C}$ is then infinitesimal. Therefore *the dew line MC of the mixture having a concentration $x_{,}$ is tangent to the critical line yC, at the critical point $y_{,}$ of this mixture; and, furthermore, the dew line falls as it sets out from its point of contact with the critical line.* Since $\mathfrak{X}$ is any concentration whatever, and since the same is true of the concentration $x_{,}$, which lies indefinitely near it, the preceding theorem is general. It may be demonstrated in an analogous manner *that the dew line of any mixture whatever is tangent to the critical line at the critical point of this mixture, and that the dew line rises as it leaves this point.*

These theorems involve the correctness of the propositions advanced by Kuenen, the dew line and the boiling line of a mixture with an assigned concentration meet at and continue together from the point where they touch the critical line.

At temperatures far from the critical temperature the dew line and the boiling line both rise from left to right, and the boiling line of the mixture having a given concentration lies above the dew line of this mixture; one must conclude that together they form in general a line having the aspect represented in Fig. 10.

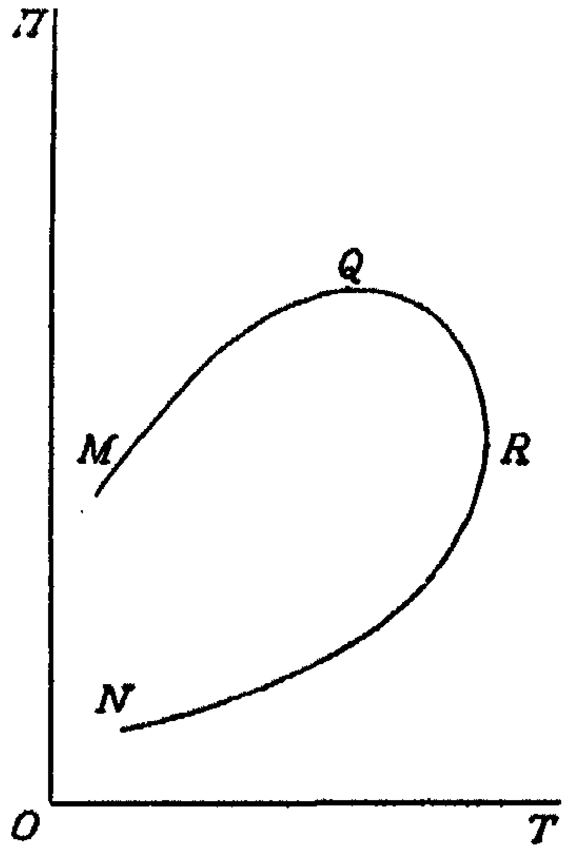

Fig. 10.

This line can have at Q a tangent parallel to the axis OT, and at R a tangent parallel to the axis OP. The critical point C can not lie upon the branch of the curve MQ, for, in setting out from this point, the dew line rises and the boiling line falls, which is contrary to what has just been demonstrated; only two cases therefore can appear: either the critical point lies between the points Q and R, or it lies upon the branch NR.

A.—*The critical point C lies between the points Q and R* (Fig. 11).

Let us suppose that the *mixture be compressed at constant temperature. If the temperature is lower than the critical temperature* Θ, the mixture is at first entirely in the gaseous state; when the pressure becomes equal to the ordinate of the dew line, the first drop of liquid appears; that portion of the mixture which is in the liquid state increases with the pressure; when the pressure becomes equal to the ordinate of the boiling line the mixture is entirely in the liquid state; it then remains homogeneous however great the pressure may become.

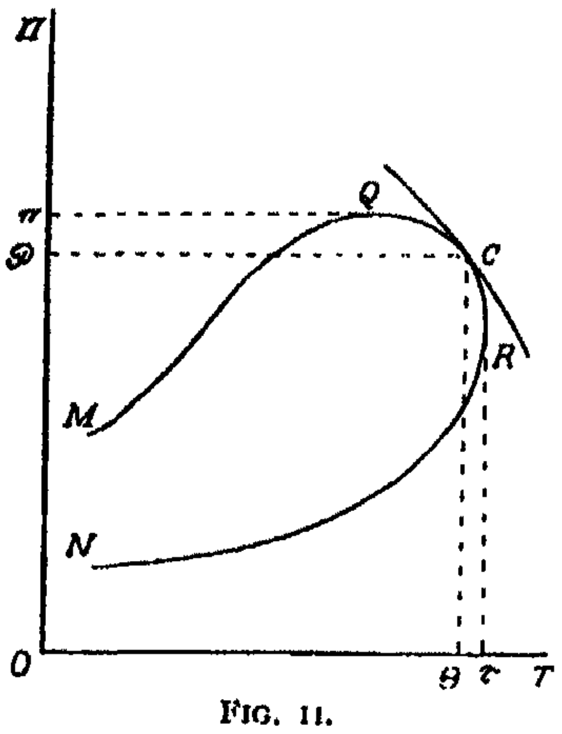

Fig. 11.

If the temperature lies between the *critical temperature* Θ and the abscissa τ of the point R, the mixture is at first in the state of a homogeneous gas; when the pressure becomes equal to the first ordinate of the dew line the first drop of liquid appears; that fraction of the mixture which is in the liquid state is at first an increasing function of the pressure; it then passes through a maximum and becomes a decreasing function of the pressure; when the pressure becomes equal to the second ordinate of the dew curve, the last drop of liquid disappears; the mixture remains then in the state of homogeneous gas however great the pressure may become. This is the experimental result of Cailletet.

If the temperature is greater than the abscissa τ *of the point R the mixture will remain homogeneous under all pressures.*

Let us now suppose *that the mixture be taken in a homogeneous liquid state and that it be heated under constant pressure.*

If the pressure is less than the critical pressure $\mathfrak{P}$, the mixture will remain at first in the state of a homogeneous liquid; when the temperature becomes equal to the abscissa of the boiling line the first bubble of gas will appear; that fraction of the mixture which is in the gaseous state will increase with the temperature; at the moment when the temperature becomes equal to the abscissa of the dew line the last trace of liquid will disappear; the mixture will then remain homogeneous at all temperatures.

If the pressure lies between the critical pressure $\mathfrak{P}$ *and the ordinate* π *of the point Q* the mixture will remain at first in the state of a homogeneous liquid. When the temperature becomes equal to the first abscissa of the boiling line, the first bubble of gas will appear; that fraction of the mixture which is in the gaseous state is at first an increasing function of the temperature; it passes then through a maximum and becomes a decreasing function; when the temperature becomes equal to the second abscissa of the boiling line the last trace of gas disappears; the mixture then remains homogeneous at all temperatures.

If the pressure is greater than the ordinate π *of the point Q* the mixture is homogeneous at all temperatures.

B.—*The critical point C lies upon the branch NR* (Fig. 12).

Let us suppose *that the mixture be compressed at constant temperature.*

If the temperature is lower than the critical temperature Θ, the mixture is at first in the state of a homogeneous gas; when the pressure becomes equal to the ordinate of the dew line, the first drop of liquid appears; that fraction of the mixture which is in the liquid state is an increasing function of the pressure; when the pressure becomes equal to the ordinate of the boiling line the mixture is entirely in the liquid state; it remains then homogeneous under all pressures.

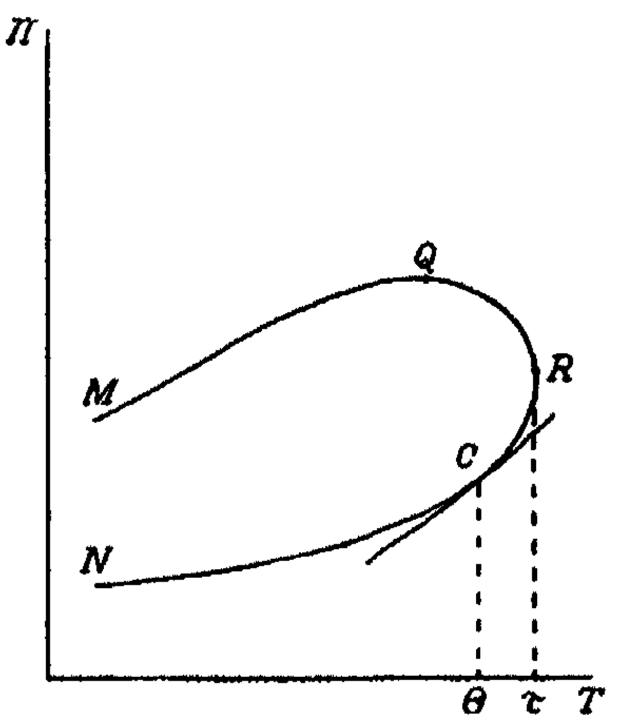

FIG. 12.

If the temperature lies between the critical temperature Θ *and the abscissa* τ *of the point R*, the mixture, under low pressures, is in the state of a homogeneous gas; at the moment when the point

(T, Π) leaves the critical line it passes without discontinuity into the state of a homogeneous liquid; the pressure, continuing to rise, becomes equal to the first ordinate of the boiling line, and at this instant the first bubble of gas appears; that fraction of the mixture which is in the gaseous state is at first an increasing function of the pressure; it passes next through a maximum and then becomes a decreasing function of the pressure; when the pressure becomes equal to the second ordinate of the boiling curve, the mixture is again entirely in the liquid state; it remains then homogeneous under all pressures.

If the temperature is higher than the abscissa τ of the point R the mixture remains homogeneous under all pressures.

If the mixture be heated under constant pressure the phenomena observed will be the same as those noted under **A.**

Let us pass now to the Second Case, as defined upon page 287 without repeating, for this case, the reasoning which has been developed concerning the first. It will suffice to indicate the result to which the reasoning leads:

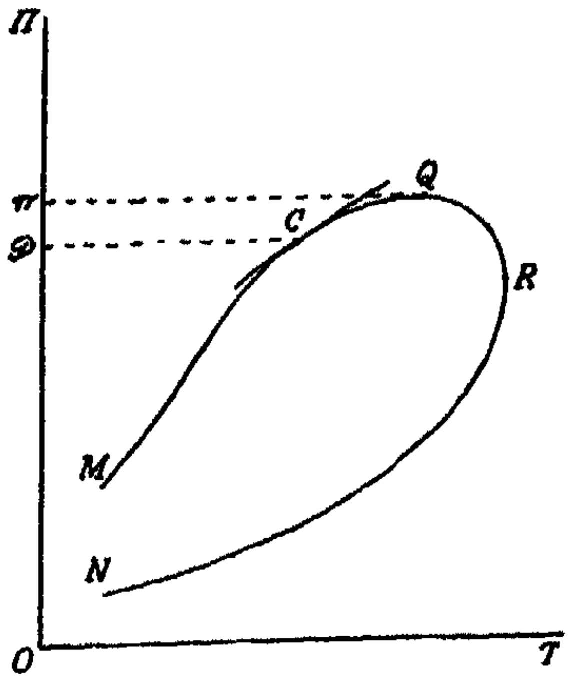

FIG. 13.

The dew line and the boiling line meet at the critical point in such wise as to prolong each other; further, the dew line in setting out from the critical point rises, while the boiling line descends; and, finally, at the critical point these two lines are tangent to the critical line.

Let us consider (Fig. 13) the line $MQRN$ formed by the boiling line and the dew line. According to the foregoing proposition the critical point C lies certainly upon the branch MQ.

Let it be supposed that the gaseous mixture is compressed at a constant temperature; exactly the same phenomenon will be observed as under the first case, **A.**

Suppose however *that the system is heated under a constant pres-*

sure. If the constant pressure is less than the critical pressure $\mathfrak{P}$, the mixture is at first entirely in the liquid state ; the temperature rises and reaches a value equal to the abscissa of the boiling line, and at this moment the first bubble of gas appears ; that fraction of the mixture which is in the gaseous state increases with the temperature ; when the temperature becomes equal to the abscissa of the dew curve the last trace of liquid disappears from the system, which then remains in the state of a homogeneous gas.

If the constant pressure lies between the critical pressure $\mathfrak{P}$ *and the ordinate* π of the point Q, the mixture is at first homogeneous and gaseous ; the temperature, rising, reaches a value equal to the first abscissa of the dew curve, and at this moment a drop of liquid appears in the system ; the mass of the liquid is at first an increasing function of the temperature ; it passes then through a maximum and becomes a decreasing function ; when the temperature becomes equal to the second abscissa of the dew line the last trace of liquid disappears from the system, which then remains in the state of a homogeneous gas. *If the constant pressure is greater than the ordinate* π *of the point* Q, the mixture remains homogeneous at all temperatures.

The three arrangements represented in the figures 11, 12 and 13 are realized for the mixture of ethane and of nitrous oxid recently studied by Kuenen ; one has to do with either one or another of these arrangements according to the value of the concentration.

It should be remarked, however, that these results can not be deduced solely from the general theorems concerning double mixtures, they require in addition a special hypothesis which has here been carefully emphasized.

It seems to me that these considerations, joined to the researches of van der Waals, to those of Kuenen and to my own early investigations, clear up completely the peculiarities which appear in the liquefaction of a mixture of two gases.

Sept. 7, 1896.

MERCURIC CHLORID

BY D. MC INTOSH

Etard[1] found that the solubility curves for mercuric chlorid in different solvents were usually composed of two branches meeting at an angle, the temperature at which the intersection occurred varying with the solvent. Etard mentions the fact that the precipitate has a different crystalline form at high temperatures from that at ordinary temperatures ; but he made no attempt to determine what two solid phases were in equilibrium at the quadruple point. Since no compounds of mercuric chlorid with water or any of the alcohols seem to be mentioned in the text-books, the natural assumption was that the two sets of crystals were two allotropic modifications of mercuric chlorid and this interpretation has been suggested by Ostwald[2]. This seemed the more plausible since two modifications of mercuric chlorid are known. On the other hand Nernst[3] has given a very satisfactory proof that the inversion temperature for two allotropic modifications cannot be a function of the solvent. At the suggestion of Professor Bancroft I have determined what actually happens when mercuric chlorid is added in excess to methyl alcohol. This solvent was selected because Etard's measurements showed that the two solubility curves intersected at about 38°.

The methyl alcohol was supplied by Bender and Höbein. It was treated with dehydrated copper sulfate and subjected to fractional distillation. It was found that above 40° small chunky crystals precipitated from the solution. These are identical in form with the crystals which separate from an aqueous solution of mercuric chlorid and are the anhydrous salt. Below 35° needles crystallize from the solution. These are an alcoholate with a composition cor-

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[1] Comptes rendus, **114**, 112 (1892); Ann. chim. phys. (7) **2**, 555 (1894).

[2] Zeit. phys. Chem. 9, 153.

[3] Theor. Chem. 505.

responding to the formula $HgCl_2,CH_3OH$. This was shown by direct analysis of the crystals after they had been pressed between filter paper. This method, though the usual one, is not very satisfactory in that almost any value may be obtained by stopping the drying process at a suitable moment. The formula was confirmed by analyzing the crystals according to a method which I have never seen described though it has doubtless been used before.

There is always heat evolved when a solid unites with a vapor to form a solid compound because the new compound is less stable at high than at low temperatures. On the other hand most solids are more soluble at high than at low temperatures and therefore dissolve with absorption of heat. Applying these two principles to the case in point, it is clear that if we add to a weighed quantity of mercuric chlorid a little less than an equivalent quantity of methyl alcohol, there will be an evolution of heat and the temperature of the mass will rise. If the system be allowed to return to its original temperature and about half an equivalent of methyl alcohol be added, the temperature will rise if the compound is $HgCl_2,2CH_3OH$ and will fall if it is $HgCl_2,CH_3OH$. By taking sufficiently large quantities of the salt, there is no theoretical reason why this method should not give results to any desired degree of accuracy. It is clear that the method can be applied only to compounds which reach a state of equilibrium quickly. With thorium sulfate or ferric chlorid it would not be successful. If the compound is less soluble at high than at low temperatures the method could not be used because there would be an evolution of heat under all circumstances.

Having shown that mercuric chlorid can crystallize with one of methyl alcohol, it seemed desirable to determine the temperature of the quadruple point with more accuracy than could be obtained by extrapolating from Etard's solubility measurements. Since the solubility of the mercuric chlorid alcoholate changes very rapidly with the temperature and that of the anhydrous salt very slowly, there is no difficulty in determining by the eye the point at which the needle-like crystals first appear. The other and more accurate method is to determine the temperature at which the thermometer reading remains constant for a definite interval of time. By these two methods the inversion temperature was found to be 38.8°. Addition of water lowers the partial pressure of the alcohol and the inversion temperature of the alcoholate. A few determinations have been made with known solutions of methyl alcohol and water by weight. Since the system, mercuric chlorid, alcoholate, solution and vapor, has one degree of freedom when the solution contains water, the thermometer reading will not remain absolutely constant while the mercuric chlorid is taking up alcohol of crystallization ; but this introduces no serious error since the temperature, at which the rate of cooling changes discontinuously, can be determined without difficulty. The results of my measurements are given in Table I, where x_1 denotes grams of water in one hundred grams of methyl alcohol and water ; x_2 denotes grams of water in one hundred grams of methyl alcohol ; x_3 denotes reacting weights of water in one kilogram of methyl alcohol.

Table I

Temp.	x_1	x_2	x_3
38.8°	0.0	0.0	0.0
36.4	2.3	2.4	1.3
34.0	4.4	4.6	2.6
33.6	4.6	4.8	2.7
33.1	4.8	5.0	2.8
32.6	5.7	6.0	3.4
30.3	7.6	8.2	4.6
22.0	16.1	19.2	10.7

Since nothing is known about the change in the solubility of mercuric chlorid on addition of water it is not worth while to attempt to apply the van 't Hoff formula to this case. Attention is called to the fact that for temperatures above 30° the lowering of the inversion point is very nearly proportional to the amount of water added. Judging from Etard's solubility determinations it is safe to conclude that mercuric chlorid can form solid compounds with methyl, ethyl and propyl alcohol, acetone and acetic acid. The break when water is solvent comes at 115° and is very probably due to the appearance of a second modification of mercuric chlorid.

Cornell University.

MASS LAW STUDIES, I

BY S. F. TAYLOR

When salts are precipitated by alcohol the exponent in the Mass Law formula is independent of the temperature so far as is yet known. There have been no experiments made to show whether this is or is not true when both the two non-miscible substances are liquids at the temperature of the experiment. For this reason I have determined the conditions of equilibrium for benzene, water and ethyl alcohol at three temperatures. The benzene used was dried over sodium and subjected to fractional distillation ; the alcohol was treated with copper sulfate ; the water was the distilled water of the laboratory. In all cases five cubic centimeters of alcohol were taken. The experiments were made in test tubes, one, two, three, four and five cubic centimeters of benzene being added to the five cubic centimeters of alcohol and water run until the solutions were saturated. To obtain the remaining data two, three, four and five cubic centimeters of water were added to the alcohol and benzene run in to saturation. The temperatures were kept con-

TABLE I

Temperature 20°

$x^{1.85}y = C \quad \log C = 0.775$

y found	y calc.	x found	x calc.	log C
5.00		1.08	1.10	0.761
4.00		1.25	1.24	0.778
3.00		1.47	1.45	0.786
2.00		1.80	1.80	0.773
1.65	1.65	2.00	2.00	0.774
1.00	1.02	2.60	2.63	0.768
0.77	0.78	3.00		0.768
0.46	0.46	4.00		0.778
0.31	0.30	5.00		0.784

stant by means of a Reichert gas regulator. The data are given in Tables I-III. In the formula x denotes cubic centimeters of water, y cubic centimeters of benzene in five cubic centimeters of alcohol. Under the heading «calc.» are the values required by the formula for the «found» values of the other components, C being given. In the fifth column are the values obtained by substituting the experimental data in the formula and solving for log C.

TABLE II

Temperature 25°

$x^{1.85}y = C \quad \log C = 0.812$

y found	y calc.	x found	x calc.	log C
5.00		1.15	1.15	0.811
4.00		1.31	1.30	0.818
3.00		1.51	1.52	0.807
2.00		1.90	1.89	0.815
1.75	1.80	2.00	2.03	0.800
1.00	1.00	2.75	2.75	0.812
0.85	0.85	3.00		0.811
0.50	0.50	4.00		0.814
0.32	0.33	5.00		0.798

TABLE III

Temperature 35°

$x^{1.85}y = C \quad \log C = 0.890$

y found	y calc.	x found	x calc.	log C
5.00		1.26	1.27	0.884
4.00		1.43	1.43	0.887
3.00		1.68	1.68	0.894
2.15	2.15	2.00	2.00	0.889
2.00	1.97	2.10	2.08	0.882
1.03	1.02	3.00		0.895
0.62	0.60	4.00		0.907
0.42	0.39	5.00		0.916

The experiments at the three temperatures can be represented by a single equation, in which the exponent is independent of the temperature and only the equilibrium constant changes. It is not safe to generalize from this one experiment and to conclude that the exponent is independent of the temperature with all pairs of non-miscible liquids; but it makes such a conclusion not impossible. In the application of the Mass Law to chemical reactions it is well known that the exponents do not change with the temperature. If the same relation should be shown to hold for physical reactions, it would simplify the task of determining the significance of the exponential term.

Professor Bancroft has published a series of measurements for the system, benzene, water and alcohol, at 20° His results could be expressed by the general formula $x^ny = C$; but he found that $n = 1.60$ while my measurements are best represented on the assumption that $n = 1.85$. There is also a great difference in the absolute solubilities, my alcohol apparently having a much greater solvent power than his. The cause of this discrepancy will be the subject of further investigation.

Cornell University, December.

NEW BOOKS

Electrophysiology. *W. Biedermann. Translated by F. A. Welby. Vol. I. Large octavo, xii and 522 pages. The Macmillan Company. New York. 1896. Price $5.50.* This is a most interesting book. Osmotic pressure phenomena are met with in the action of the «physiological salt solution»; in the behavior of the frog's sartorius, page 67; to a certain extent in the action of dilute acids and strong alcohol upon muscle fibre, pages 44, 49; possibly also in the selective coloring of certain dyestuffs. It is interesting to read on page 52 that «the rule for each single, turgescent, colourable mass is that it stains more intensely in proportion as it contains less water of imbibition». On page 91 we find a relation between reaction velocity and temperature; on page 96 a peculiar case of catalytic action. On pages 107, 110 and 220 we meet the specific effects of sodium, barium and potassium as ions though with sodium the effect seems often to be counterbalanced by the anion. On page 211 it is surprising to learn that anode and cathode could ever be misleading terms. The swelling caused by the electric current, page 302, the behavior of Infusoria, page 307, and the difference between muscle and protoplasm, page 306, are problems which appeal to the chemist who will also be fascinated by the question raised by Hermann's postulate, page 351, that «dying substance is negative to living substance.» Of more general interest is the influence of vibrations upon tetanus and the lay reader would have welcomed a note on the possibility or impossibility of utilizing this to prevent death by lock-jaw.

These few, brief references suffice to show that the day is not far distant when a knowledge of physical chemistry will be an essential part of a physiologist's education, while the physical chemist will have to study physiology if he wishes to keep up with the development of his subject.

The book is remarkably free from errors and the translation is well done. The reviewer has noticed the following shortcomings: On page 107 there is Na_2CO_2 and on page 222, Na_2Cl_3 instead of Na_2CO_3 while Becquerel's name is misspelled on page 299. Kathode is German and not English. In places it is not clear whether the author distinguishes between intensity of current and current density though the latter term is used correctly on page 271. On pages 211 and 271, there is a needless repetition while the account of du Bois-Reymond's method of determining electromotive forces, page 335, is unsatisfactory. In a book of this sort one does not like to see P.D. written for potential difference and there are no circumstances which make it pardonable to refer to du Bois-Reymond as du Bois. *Wilder D. Bancroft.*

Studies in Chemical Dynamics. *J. H. van't Hoff; revised and enlarged by Ernst Cohen and translated by Thomas Ewan. Large octavo, vi and 286 pages. Chemical Publishing Co., Easton, Pa.; Frederick Muller and Co., Amsterdam; Williams and Norgate, London. 1896. Price $2.50.* We would call attention to the appearance of an English version of van 't Hoff's revised *Études*, whose recent appearance in German was chronicled in this Journal **1**, *107* (*November*), where a characterization of its contents is presented. The translator says: «The appearance of this edition seemed to provide a wished-for opportunity of introducing the book to a wider circle of English readers by means of a translation; the paucity of works in our language dealing with the subject made this the more desirable.

«The simplicity and originality of the treatment of chemical change and affinity make the book of the greatest value to the student seeking clear views on the fundamental problems of our science, whilst the fertility in ideas makes it uncommonly suggestive to the chemist already familiar with the outlines of the subject.»

The translator is, fortunately, one who has contributed important features of the work which is presented, and he has given us a good rendering. The German edition and the English translation are remarkably alike in outward appearance, they seem in fact to have passed through the same printing office, in Holland. Both the translation and the printing have been done well, so that we have here to do with a valuable addition to an important and very interesting branch of chemical literature. *J. E. Trevor.*

Higher Mathematics. *Edited by Mansfield Merriman and Robert S. Woodward. Octavo xi and 576 pages. John Wiley and Sons; New York. 1896. Price $5.00.* For the reason that in the best American colleges the study of mathematics is continued by many students after they have completed a general course in the calculus it has seemed desirable to prepare a text book which shall assemble for the purposes of such further study a series of articles on various important mathematical subjects. Such a book is the one before us. Each of its chapters is complete in itself and is intended primarily to present the leading principles of its topic. Each one has been written by a distinguished specialist in the field which it treats, and although the authors have been guided by certain general instructions, yet each adopts his own form of presentation,—some for example pursue the formal plan which is customary in text books while others use the historical method.

The appearance of the book is timely in many ways. Something of the kind is seriously needed by the physical chemist who has not had an exceptional mathematical training, for the constant and ever increasing employment of the higher mathematical methods in his subject often require him, if he will be thorough, to look up the simpler elements of such topics as differential equations, determinants and the solution of cubic and quartic equations. Information of this useful kind is admirably brought together in the present work, so that it is to be warmly recommended as a reference book for practical purposes. Its several chapters are on the Solution of Equations, by Merriman of Lehigh; Determinants, by Weld of Iowa; Projective Geometry, by Halstead of Texas; Hyperbolic Functions, by McMahon of Cornell; Harmonic Functions, by Byerly of Harvard; Functions of a Complex Variable, by Fiske of Columbia; Differential Equations, by Johnson of the U. S. Naval Academy; Grassman's Space Analysis, by Hyde of Cincinnati; Vector Analysis and Quaternions, by Macfarlane of Lehigh; Probabilities and Theory of Errors, by Woodward of Columbia; and History of Modern Mathematics, by Smith of the Michigan State Normal School.

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 which bear upon any phase of Physical Chemistry.

General

Note on Different Forms of the Entropy Function. *W. F. Durand. Phys. Rev.* 4, *343* (*1897*). The author recalls that the heat $\int dQ$ absorbed in a reversible change is not a function of the end conditions, so dQ is not a complete differential but may be reduced to one by the integrating factor $1/T$. The existence of one integrating factor connotes the existence of an indefinite number of them, so writing β for any one we have $\int \beta dQ = \eta$, the corresponding entropy function.

Assume an auxiliary function P, of the variables fixing the state of the system, such that it shall be constant in adiabatic changes; η is so likewise, so each is a function of the other. For simplicity the discussion is limited to cases with two independent variables, p and v being chosen. Using this auxiliary we have

$$dQ = \frac{\partial Q}{\partial P} dP \qquad (1)$$

where $\partial Q/\partial P$ is a function of p and v and may be written

$$\frac{\partial Q}{\partial P} = f(p,v)F(P) \qquad (2)$$

where the form of f depends upon that taken for F. So

$$\frac{dQ}{f(p,v)} = F(P)dP \qquad (3)$$

where the second member, and therefore the first, are complete differentials, so $1/f(p,v)$ is an integrating factor and the members of (3) equal $d\eta$. So

$$\beta = F(P)\frac{\partial P}{\partial Q} \qquad (5)$$

where the form of F is unlimited. One may express β in terms of other differential coefficients, *e.g.*, for constant pressure

$$\left(\frac{\partial Q}{\partial P}\right)_p = \left(\frac{\partial Q}{\partial T}\right)_p\left(\frac{\partial T}{\partial v}\right)_p\left(\frac{\partial v}{\partial P}\right)_p = f(p,v)F(P)$$

$$\beta = \frac{F(P)}{\left(\frac{\partial Q}{\partial T}\right)_p\left(\frac{\partial T}{\partial v}\right)_p\left(\frac{\partial v}{\partial P}\right)_p}\ .$$

It is then shown, as illustration, that for a gas for which $pv = RT$:—

Assuming $F(P) = c_v/P$, then $\beta = 1/T$ and $\eta = c_v \log(pv^\gamma)$;
Assuming $F(P) = c_v/R$, then $\beta = v^{\gamma-1}$ and $\eta = Tc_v v^{\gamma-1}$;
Assuming $F(P) = c_v P^{1/\gamma-1}/R$, then $\beta = p^{1/\gamma-1}$ and $\eta = \gamma T c_v p^{1/\gamma-1}$.

In the second and third forms the integrating factoris expressed simply as a function of v or of p. Finally, $1/T$ is an integrating factor for all systems, because it defines the temperature scale; $v^{\gamma-1}$ or another function of v, or one of p, cannot be so because we can not arbitrarily fix a corresponding scale of volumes or of pressures. Further, « while $1/T$ is an integrating factor for all substances, the expression of its value as a function of p and v will vary according to the substance ». The reviewer would add that another phase of this same subject has been treated beautifully by Budde, Wied. Ann. **45**, 751 (1892). *J. E. T.*

On Energetics. *L. Boltzmann. Wied. Ann.* **58**, *595 (1896).* This article apparently closes the interesting discussion on Energetics, which arose among Boltzmann, Helm, Planck and Ostwald after the Lübeck address of the last. The matters in discussion with Helm and Planck are now cleared up, but Boltzmann expresses himself as yet unable to see how a system of Mechanics can be constructed from the kinetic energy of motion as the primary idea, with the moving thing as a derived one. He shows moreover how the Energetics of Helm, in reaching the Lagrangian equations from transformation of the rectangular coordinates of material points and of the forces acting upon them, involves the assumption that bodies are systems of material points, and that then, by continued motion under the influence of forces not working uniformly upon all the points, irregular motions of them must arise whereby apparent kinetic energy is lost, and with sufficiently violent motion the points will creep past one another, in a fusion, and some will escape, in vaporization, and we recognize the kinetic-molecular hypothesis again in a new form.

Concerning Ostwald's reply it is remarked that since in the latter's scheme of Mechanics the old ideas are retained it is hardly essential whether the mass or the energy or neither one is to be regared as the substance coming in question. As to the alleged unfruitfulness of the *Atomistik* it is urged that much of modern science has been reached with its aid,—and that, finally, the mathematical part of the theory of gases aims chiefly at a development of mathematical method, an aim which lies outside the scope and therefore of the range of criticism of the purely practical experimenter. The reviewer would add that Boltzmann cites the past usefulness of the molecular hypothesis without reckoning its sins, and too that the former may well be granted by those who now maintain the hypothesis to be outworn. *J. E. T.*

An Ideal Chemical Laboratory. *W. Ramsay. Chem. News.* **74**, *312 (1896)*. This is an address delivered at the opening of the Gossage laboratory, Liverpool. Professor Ramsay believes in a small laboratory so that the chief may know each man and that there may be a community of interests. He believes also in a not too luxurious laboratory. While the reviewer thinks that a chemist should be able to make his own tools he can see no reason why the advanced student should do so. It would seem also that a man should not find it very difficult to keep ten students busy at research work. On the other hand the reviewer agrees fully with the statement that chemical students are much overtaught. They should be helped to learn and not taught at all. *W. D. B.*

The New Elements of Clèveite Gas. *J. R. Rydberg. Astrophys. Jour. 4, 91 ; Wied. Ann.* **58**, *674 (1896).* The author applies his method of analysis to the data obtained by Runge and Paschen for the spectrum of the Clèveite gas and finds as they had found—proof of the existence of the two gases, helium and parhelium.

W. D. B.

The Unit of the Atomic Weights. *K. Seubert. Zeit. anorg. Chem.* **13**, *229 (1896).* The combining weights of the elements have been recalculated, using Morley's value for the ratio between oxygen and hydrogen. The author considers that this ratio is definitely determined and claims that there is now no reason why the combining weight of hydrogen should not be taken as equal to unity.

W. D. B.

On the Homogeneity of Argon and Helium. *W. Ramsay and J. N. Collie. Proc. Roy. Soc.* **60**, *206 ; Comptes rendus,* **123**, *214, 542 (1896).* No change in argon was produced by fractional diffusion. With helium the same process yielded two gases having identical spectra but densities of 1.874 and 2.133 respectively. The authors are of the opinion that in fractional diffusion they have found a substitute for Maxwell's «demons». *W. D. B.*

The Atomic Weights of Nitrogen and Arsenic. *J. G. Hibbs. Jour. Am. Chem. Soc.* **18**, *1044 (1896).* For O = 16.00 the author finds N = 14.0003 and As = 74.9158. *W. D. B.*

The Alleged New Element, Lucium. *W. Crookes. Chem. News.* **74**, *259 (1896).* Lucium proves to be impure yttrium.

W. D. B.

Monovariant Systems

On the Dependence of Solubility on Pressure. *E. von Stackelberg. Zeit. phys. Chem.* **20**, *337 (1896).* After a short discussion of previous work the author gives the formulas of van Laar and of Braun for the variation of solubility with pressure and temperature and shows that they are consistent with each other. The formulas are next reduced to form for computation. The experiments were carried on by compressing saturated solution and powdered salt in a steel block by a Cailletet pump, the solution was stirred by a magnetic stirrer composed of an iron frame moved by the action of a coil outside the block. After an experiment in which the solution was under pressure for an hour or two the pressure was removed and some of the solution taken out as quickly as possible for analysis. The pressures used were 0 and 500 atm. The salts used were NaCl, NH_4Cl and $KAl(SO_4)_2$ as obtained from Kahlbaum. The changes in solubility found from the experiments are compared with those computed by the formulas and are found to be smaller than the computed values. This may come from inaccuracy in the constants used in the computations or more probably from the errors of the experiments. *E. B.*

On the Behavior of the Halogen Acids at Low Temperatures. *T. Estreicher. Bull. Acad. Cracovie* **1896,** *325 ; Zeit. phys. Chem.* **20,** *605 (1896).* Determinations with a helium thermometer :

HCl	melts at	− 111.1°,	boils at	− 83.7°	under 745.2 mm
HBr	melts at	− 87.9 ,	boils at	− 64.9	under 738.2
	freezes at	− 88.5 ,	crit. temp.	+ 91.3	
HI	melts at	− 50.8 ,	boils at	− 34.14	under 730.4
	crit. temp.	+ 150.7 ,	boils at	34.12	under 739.8

J. E. T.

Researches on the Dissociation of Hydrated Salts and Similar Compounds. *Tenth Paper. H. Lescoeur. Ann. phys. chim.* (7) **9,** *537 (1896).* The dissociation pressures of hydrated potassium carbonate, borax, sodium hyposulfite, potassium ferrocyanid, potassium oxalate and potassium bicarbonate were determined. The experiments with potassium carbonate, alcohol and water do not prove the existence of an alcohol hydrate. They show that $K_2CO_3 2H_2O$ can exist in equilibrium with aqueous alcohol containing from 90.8 to 97.7 per cent of alcohol by weight. With more concentrated alcohol the hydrate effloresces ; with more dilute alcohol a second solution phase appears. *W. D. B.*

On the Liquation of Certain Alloys of Gold. *E. Matthey. Proc. Roy. Soc.* **60,** *21 (1896).* Reviewed in this Journal **1,** 62 (1896).

W. D. B.

The Freezing-points of Dilute Aqueous Solutions. III. *E. H. Loomis. Phys. Rev.* 4, *273* (*1897*). Measurements were made with the mean temperature of the room about + 3° thus making the experimental error of the work one-half what it had previously been. The molecular depression of the freezing-point passes through a minimum at about *n*/10 in the case of all chlorids. The author discusses his results from the point of view of the dissociation theory; but he is badly handicapped in the cases of $SnCl_4$, Na_2HPO_4, Na_3PO_4, *etc.* by not being familiar with anything except conductivity and cryoscopic measurements. No reference is made to the work of Hittorf or Shields.
W. D. B.

On the Determination of Freezing-points. *J. A. Harker. Proc. Roy. Soc.* **60**, *154* (*1896*). Instead of determining the zero of a thermometer by placing it in melting ice the author suggests the use of the Beckman cryoscopic method.
W. D. B.

Complete Freezing-point Curves of Binary Alloys containing Silver or Copper, together with Another Metal. *C. T. Heycock and F. H. Neville. Proc. Roy. Soc.* **60**, *160* (*1896*). An abstract giving no data and no diagrams. Complete freezing-point curves were determined for Ag with Cu, Pb, Sn and Sb; for Cu with Pb and Sn; while parts of the curves were measured for Bi, Pt, Au, Al and Tl in silver, and for Bi, Cu, Ni, Fe and Al in Cu. The discussion of the results must be postponed until the data are published.
W. D. B.

Divariant Systems

An Attempt to Liquefy Helium. *K. Olszewski. Wied. Ann.* **59**, *184* (*1896*). The work was done with 140 c.c. helium from clevite, sent by Ramsay and containing no gas removable by Mg, CuO, P_2O_5 or NaOH. Its low density (2.133 referred to hydrogen), ‹monoatomicity› ($c_p/c_v = 1.652$) and low solubility in water (*0.7* c.c. in *100*) indicated great permanence, so the first experiments were made with liquid oxygen.

In the first series the gas was cooled to − 210°, the vapor pressure of oxygen under 10 mm pressure, and compressed to 125 atm;

no liquefaction ensued, even under sudden expansion to 1 atm. About one per cent of a white body was separated during compression. In the second series, reduction of the pressure of liquid oxygen in an outer tube cooled air in an inner one where the helium tube stood; with this air boiling against 10 mm pressure, at − 220°, the pressure of the helium was lowered rapidly from 140 atm to 1, but no clouding ensued. The attempt was accordingly unsuccessful, helium is more permanent than hydrogen.

The temperature reached in the first series of adiabatic expansions was then calculated by the Laplace-Poisson equation

$$T/T_1 = (p/p_1)^{(k-1)/k}$$

where the indices indicate the temperature and pressure values reached by the expansion, and their absence the initial values; expansion to one atmosphere gave − 263.9°C = 9.1° absolute, the lowest temperature yet reached,—the boiling temperature of helium is accordingly over twenty degrees below that of hydrogen. Helium thermometers are therefore to be recommended for measuring temperatures below the critical temperature of hydrogen, − 234.5°. The author compares, finally, the temperature of oxygen with its vapor under different pressures, as found by such a thermometer, with those found by Estreicher with a hydrogen thermometer—the agreement is as good as perfect.

The paper contains a paragraph on the boiling out of nitrogen from air; air thus made richer in oxygen remains homogeneous under 10 mm, about six degrees below the freezing temperature of nitrogen, while unchanged air under this pressure separates crystallized nitrogen. Dewar is wrong in asserting the air to freeze as such. An interesting page of footnote reviews the recent controversy with Dewar. It may be noted in connection with this work that Kuenen and Randall (Proc. Roy. Soc. **49**, 60) have determined the coefficients of expansion of argon (0.003665), helium (0.003668), air (0.003663) and of hydrogen, brought successively into the same thermometer. *J. E. T.*

On the Characteristics which Determine the Course of the Curve of Folding in the Case of a Mixture of Two Substances. *J. D. van der Waals. Arch. néerl.* **30**, *266* (*1896*). The «curve of folding » is the locus of the points representing the relation between the critical temperatures and pressures of a two-component, two-phase mixture of variable composition ; it is so named because the corresponding volumes and compositions are determined by the point of folding [where the bitangent plane becomes singly tangent, see Korteweg, *Arch. néerl.* **24**, 57] of the V, x, ψ-surface, —x and $1-x$ give the percentage composition of the phase, V, ψ and η its specific volume, free energy and entropy. The equation of this line is unknown, but its differential equation is shown to be

$$\frac{dp}{dt} = \left(\frac{\partial^2\eta/\partial x^2}{\partial V^2/\partial x^2}\right)_{p,t}$$

and the chief characteristics of the curve are sought therefrom. After eliminating the derivative $\partial^2\eta/\partial x^2$ with the aid of

$$t\,d\eta = d\varepsilon + p\,dV - (\partial\psi/\partial x)_{vt}\,dx$$

it is shown that the « line of equal pressure » is, save in exceptional cases, tangent to the spinodal line [the limit separating the concavo-convex parts of the surface from those concave or convex only] at the point of folding, and that the line of folding is tangent to and terminates the line of maximum or of minimum pressures where it meets the latter. It is shown also that $(\partial^2 v/\partial x^2)$ indicates a point of folding and that then $dp/dt = \infty$. These two special points of the curve of folding have been encountered by Kuenen with mixtures of N_2O and C_2H_6,—the latter's belief in a discontinuity at them must be wrong. The remainder of the paper is occupied by further conclusions resting upon the assumption that a, the attraction constant of van der Waals's equation is independent of x. *J. E. T.*

On the Theory of Corresponding States. *G. Bakker. Zeit. phys. Chem.* **21**, *127* (*1896*). The author combines his formula (see this Journal **1**, 248).

$$\rho = a(\delta_1 - \delta_2)$$

where ρ is the specific inner heat of vaporization and δ_1 and δ_2 are the densities of liquid and saturated vapor, with $dp/dT = \rho/(v_2 - v_1)T$ and van der Waals's theory of the ‹corresponding states› to obtain

$$\frac{\mu\rho}{T_k} = f_2\left(\frac{v_k}{v_1} - \frac{v_k}{v_2}\right)$$

where μ is the molecular weight, critical values are indicated by the subscript k, and f_2 has the same value for all bodies for which the law of corresponding states holds. The law of van der Waals for the heat of vaporization,

$$\mu r / T_k = f(T/T_k)$$

r being the heat of vaporization, follows from it. To get the same result more generally he reads from

$$(\partial\eta/\partial v)_T = (\partial p/\partial T)_v$$

and the van der Waals theorem, that the isothermal molecular changes of entropy of all bodies remaining in corresponding states are equal; or replacing *any* change by small isothermal and adiabatic changes, whereby the entropy remains constant on the adiabatics, that in general molecular corresponding changes of entropy are equal.

It is further shown in two ways similar to the above that in corresponding changes the molecular heats and also the molecular (true heat capacities), energies and free energies are equal, and that under the same conditions the velocity of sound in a fluid is proportional to the critical temperature of the latter and is inversely proportional to its molecular weight. That the velocity of sound is the same in CO_2 and in N_2O is thus dependent not only upon the equality of the molecular weights of these gases but also upon their having nearly the same critical temperatures. *J. E. T.*

On the Theory of Corresponding States. *G. Bakker. Zeit. phys. Chem.* **21**, *507* (*1896*). In an earlier paper (*Ibid* **21**, *127*, see foregoing review) on this subject the author has tacitly assumed that when the reduced isotherms of two bodies coincide their isentropic curves do so also. He now shows this assumption to be unnecessary, discussion of the curves demonstrating readily that when for two bodies the same relation holds among the three ratios of p, v and T to the critical values of these quantities, and the values of c_p/c_v are equal in the gaseous state, then «corresponding» changes of the entropy are also equal. It is further shown that when two of the reduced «surfaces of van der Waals» coincide and c_p/c_v has the same value for both in the gaseous state, then the reduced v, η, ε -surfaces of Gibbs likewise coincide. *J. E. T.*

The Distribution of a Substance between two Solvents. *A. Stschukarew. Jour. Russ. Soc.* **28**, *I, 604* (*1896*). For the speed with which a solute passes from one solvent in which its concentration is C' into the other solvent in which its concentration is C the author writes $\partial C/\partial t = k(S - C)C'$ and for the reverse reaction $\partial C'/\partial t = k'(S' - C')C$. S' and S denote the solubilities of the solute in the first and second solvent respectively. For equilibrium we have $(S - C)C'/(S' - C')C = \mathit{constant}$, a relation which coincides with Nernst's formulation only for very dilute solutions or when $k = k'$. The author tested his formula on some data by Jakowkin and others. The result was not bad in spite of the doubtful accuracy of the premises; the solubility as defined by the author has a definitely characterized value only for the equilibrium between the solid substance and the solvent. *E. St.*

On the Distribution of a Substance between two Non-miscible Liquids. *A. A. Jakowkin. Jour. Russ. Soc.* **28**, *I, 828* (*1896*). The author points out that Stschukarew's formula (see preceding review) overlooks the thermodynamically essential point of the reacting weights of the solute in the two solvents; that it gives only a linear relation between the concentrations—which is only one case out of many; and that the conclusions drawn from the relative values of the terms $\partial C/\partial t$ and $\partial C'/\partial t$ do not accord with the facts.

E. St.

Free Hydrazin. *C. A. Lobry de Bruyn. Recueil Trav. Pays-Bas*, **15**, *174* (*1896*). Pure diamid is made by treating the hydrate with barium oxid. It melts at 1.4°; boils at 13.5° under a pressure of 761.5 mm; its critical temperature is about 380° and its critical pressure 135 atm. It dissolves salts with great readiness and forms compounds with sodium chlorid and lead nitrate. The stability of hydrazin increases with the pressure as was to be expected since the decomposition products are nitrogen, hydrogen and ammonia.

W. D. B.

Cryoscopic Investigations. *K. Auwers and K. Orton. Zeit. phys. Chem.* **21**, *337* (*1896*). An attempt to establish a relation between the structure formula of a solute and the apparent change of reacting weight with the concentration. From a study of twenty paraoxyazo-compounds and twelve orthooxyazo-compounds the authors decide that the former are phenols and the latter hydrazones. This confirms the conclusions of McPherson and of Goldschmidt and Rosell. It was found that neither with hydroxyl compounds nor with acids could the change of the reacting weight with the concentration be expressed by the ordinary dissociation formula. This statement is not necessarily accurate, because the authors have assumed tacitly that the hypothetical dissociation is independent of the temperature. *W. D. B.*

On Abnormal Depressions of the Freezing-point. *G. Bodländer. Zeit. phys. Chem.* **21**, *378* (*1896*). The author recalculates the data of Ciamician and Garelli and shows that the distribution of phenol between liquid and solid benzene can be represented by the formula: $x^{1.6}/y = 0.304$ where x and y denote the concentrations in the liquid and solid solutions respectively. It is then shown that this result may be explained by assuming a polymerization of phenol in liquid benzene. *W. D. B.*

Polyvariant Systems

Some Remarks on Aluminum Amalgam. *V. Biernacki. Wied. Ann.* **59**, *664* (*1896*). Attention is called to the fact that the mercury which is left after acting upon a substance with aluminum amalgam can be converted back into the amalgam and used indefinitely. This information is correct but not important. *W. D. B.*

Reduction of Concentrated Sulfuric Acid by Copper. *C. Baskerville. Jour. Am. Chem. Soc.* **18**, *942* (*1896*). It is shown that copper reduces concentrated sulfuric acid even at 0°, thus disproving the contrary assumption of Andrews. *W. D. B.*

Electromotive Forces

The Interpretation of Electromotive Phenomena in Living Tissue according to the Dissociation Theory of Arrhenius. *Tschagowetz. Jour. Russ. Soc.* **28**, *I*, *657* (*1896*). This unabashed invasion of electrochemistry into the realms of physiology and even of psychology starts as follows: By the exercise of a muscle or its irritation through external influences, electromotive forces appear and the products of the reaction accumulate in each active or irritated muscle. Since, without introducing any serious error, free carbonic acid may be taken as the sole substance formed, Nernst's formula

$$\Pi = \frac{u/n - v/n_1}{u + v} \frac{RT}{\varepsilon} \log \frac{p}{p_1}$$

may be applied in the form $\Pi = 0.047 \log p/p_1$ where p and p_1 are the osmotic pressures of carbonic acid at two points in the muscle. (The nitrogenous products such as urea, *etc.*, are non-conductors; those containing no nitrogen, such as lactic and phosphorous acids, differ only in the anions and these have practically the same migration velocity. In the formulas u and v are the migration velocities, n and n_1 the number of the ions. The data are: $u = 290$, $v = 40$, $n = 1$, $n_1 = 2$, $e = 96540$ *coul.*, $T = 290°$). From this formula can be deduced the two laws of L. Hermann:

I. «Quiescent, unirritated tissue is free from current», for $\Pi = 0$ when $p = p_1$.

II. «Each irritated part of a muscle is electrically negative towards a part which is not irritated». The qualitative interpretation which the author gives to this is that «the more dilute solution has the same electrical sign as the ion with the greater migration velocity» *i.e.* the parts which are not stimulated become charged positively through hydrogen ions. Hermann has shown that a muscle stimulated to its limit forms 6.5 times as much H_2CO_3 as the same muscle in a state of rest. If $p/p_1 = 6.5$ then $\Pi = 0.038 V$ while the measurements of du Bois-Reymond with non-polarizable electrodes gave the experimental value $\Pi = 0.043 V$.

When a muscle is cut slanting, the concentrations in the obtuse and the acute angles are inversely proportional to these angles, $p/p_1 = \alpha/(180 - \alpha)$. There must therefore be a potential difference between the points, and the calculated value agreed fairly well with that observed. Equally satisfactory results were obtained with conically shaped muscles. These concentration cells in living tissue can certainly be considered as a factor in the working of the sensory nerves. The author does not stop here, but connects the logarithmic increase of the electromotive force with the psychophysical law of Weber and Fechner. This is only an analogy, for the law of the logarithmic increase of the sensation with the regular increase of the stimulus refers to a secondary estimation of the stimulus according to Wundt while the measurable tetanic effects of a stimulus appear to be directly proportional. *E. St.*

Dielectrics. *R. Appleyard. Phys. Soc. Lond. Proc.* **14**, *255* (*1896*). Quantitative experiments, by the «direct reflection» method, upon the dielectric resistance of paraffin paper, mica, gutta percha and caoutchouc. It is added that on heating paraffin wax from twenty degrees below its melting temperature the resistance rapidly falls until a melting begins, when there occurs a definite fall by about two-thirds of the value then reached. The resistance thereupon remains steady until the melting is complete, to again fall steadily with continued heating. The reverse process occurs on cooling. *J. E. T.*

On O. F. Tower's «Studies on Superoxid Electrodes». *W. A. Smith. Zeit. phys. Chem.* **21**, *93* (*1896*). The writer criticises the method employed in the «studies» in question; emphasizes the difficulty of obtaining constant MnO_2 electrodes; suggests an (empirical) modification in the formula connecting the E.M.F. with the concentration of the solutions employed; and concludes that «it is only under special conditions that the superoxid electrode is available for determining the concentration of hydrogen ions.»

W. L. M.

A New Form of the Quadrant Electrometer. *T. Dolezalek and W. Nernst. Zeit. Elektrochemie*, **3**, *1* (*1896*). An attempt to increase the sensitiveness of the Thomson electrometer by fastening a Zamboni dry cell to the needle failed on account of the inconstancy of the cell. By adding lead peroxid as a depolarizor this trouble was avoided and an instrument was obtained with a sensitiveness one hundred times as great as that of the quadrant electrometer and with a capacity only about one one-millionth of that of the capillary electrometer. *W. D. B.*

On a Comparison of the Normal Resistances of the British Association with those of the Physicotechnical Imperial Institute of Berlin. *S. Lindeck. Zeit. Instrumentenkunde,* **16,** *272* (*1896*). The English ohm proves to be about 0.01 per cent larger than the German. *W. D. B.*

The Problem of Contact Electricity. *W. Nernst. Zeit. Elektrochemie,* **3,** *209* (*1896*). An extract from a paper reviewed in this Journal, **1,** 133 (1896). *W. D. B.*

The Action in the Jacques Carbon Cell. *C. J. Reed. Electrical Engineer,* **22,** *574* (*1896*). The peculiar views of the author are illustrated in the following quotation: «If the action in the Jacques cell is galvanic, that is, if the chemical action is spontaneous and not a result of electrolysis, the chemical action will continue to take place on the carbon after it has passed out of the electric circuit.» On this basis the Clark cell is really a thermopile.

W. D. B.

Electricity from Chemical Sources. *E. Andreas. Zeit. Elektrochemie.* **3,** *188* (*1896*). In the Borchers gas cell the carbon monoxid takes no part in the reaction, which consists in the oxidation of the cuprous chlorid. By using hydrogen and chlorin under pressure with carbon electrodes, the author obtained a current of one ampere with an electromotive force of 1.5 volts. The author proposes to replace the hydrogen and chlorin by sulfurous acid and oxygen, using sulfuric acid as electrolyte with carbon electrodes.

W. D. B.

Measure of the Force Acting on Non-electrified Liquid Dielectrics placed in an Electric Field. *H. Pellat. Comptes rendus,* **123,** *691* (*1896*). Experimental data confirming the author's formula.

W. D. B.

On the Interpretation of Polarization Phenomena with thin Metallic Membranes. *L. Arons. Wied. Ann.* **58,** *680* (*1896*). The experiments of Ochs and of Luggin to the effect that conduction takes place through pores in the gold leaf are shown not to be conclusive. The author made some measurements with thin platinum foil in a sulfuric acid solution and obtained results similar to those with the gold membranes. It was also shown that the foil was not pierced. The bulk of the evidence certainly favors the interpretation of Arons. *W. D. B.*

On the Continuous Change of an Electrical Property in the Film separating Solid and Liquid Substances. *F. Braun. Göttinger Nachrichten*, **1896**, *166; Wied. Ann.* **59**, *682 (1896)*. The thin film of water which forms on the surface of a gypsum plate shows a polarization which decreases with increasing thickness of film, approaching as a limit the hypothetical maximum polarization of water. *W. D. B.*

On the Changes produced in Magnetised Iron and Steels by Cooling to the Temperature of Liquid Air. *J. Dewar and J. A. Fleming. Proc. Roy. Soc.* **60**, *57 (1896)*. When magnetized iron or steel is plunged into liquid air, — 185°, there is a distinct decrease in magnetic moment, which becomes somewhat greater when the magnet is warmed to + 5°. The values for — 185° and + 5° seem to be permanent, so that the magnetic moment varies thereafter inversely as the temperature. Steel containing nineteen per cent of nickel or over is an exception and has a maximum magnetic moment at about + 56°. *W. D. B.*

On the Electrical Resistance of Bismuth at the Temperature of Liquid Air. *J. Dewar and J. A. Fleming. Proc. Roy. Soc.* **60**, *72 (1896)*. The conductivity of electrolytic bismuth shows no sign of passing through a maximum with falling temperature. The contrary results which had been obtained by the authors were undoubtedly caused by impurities in the bismuth used. The effect of a given transverse magnetic field in decreasing the conductivity of bismuth is immensely increased by cooling the bismuth to the temperature of liquid air. *W. D. B.*

On the Electrical Resistivity of Pure Mercury at the Temperature of Liquid Air. *J. Dewar and J. A. Fleming. Proc. Roy. Soc.* **60**, *76 (1896)*. The resistance of mercury was determined to temperatures as low as — 204°. By extrapolation it is seen that the resistance becomes zero at the absolute zero of temperature.

W. D. B.

Polarization and Internal Resistance of a Galvanic Cell. *B. E. Moore and H. V. Carpenter. Phys. Rev.* 4, *329* (*1897*). By a rather unsatisfactory method it is shown that there is anodic and cathodic polarization when a cell composed of zinc and carbon electrodes in a solution of ammonium chlorid is placed on short circuit. There seems to be a constant error in the measurements of over five one-hundreths of a volt. *W. D. B.*

On the Jacques Carbon Battery and on a Thermo-tropic Battery. *C. J. Reed. Jour. Franklin Inst.* **142**, *385* (*1896*). If two pieces of copper are separated by a film of copper oxid and one of the copper strips is heated in a Bunsen flame, there is set up a potential difference of about 0.4 volt. This is supposed to show that the action in the Jacques cell is thermoelectric in nature. The Jacques cell consists of carbon and iron electrodes in melted sodium hydroxid. To prevent polarization, air is blown through the electrolyte. The electromotive force of this cell is not known; but it is stated to be just under one volt. It is not clear what the connection is between Reed's thermotropic cell and the Jacques element and this criticism applies to many of the papers upon the subject. It has been shown that if the two electrodes in the modifications of the Jacques idea are at different temperatures there is a change in the electromotive force; but this applies to every voltaic cell. It has been suggested that in the Jacques cell the air forms a thin film of oxid on the iron, which is continually being reduced; but it is clear that the cathode is really passive iron and that the function of the air is to prevent the film of oxid from being reduced. The Jacques cell is a reduction and oxidation cell with the reducing agent as one electrode and passive iron as the cathode. *W. D. B.*

On Electrolytic Thermopiles. *W. Duane. Zeit. Elektrochemie,* 3, *164* (*1896*). In a symmetrical cell one junction between two solutions is heated. The author states that the resulting electromotive force can be calculated from Nernst's formula. With hydrochloric acid a maximum value is observed when the heated junction is at a temperature of 50°. The possibility of a maximum is due to the fact that the transference number approaches the value 0.5 with increasing temperature. By taking this into account 50° is calculated as the most probable value for the maximum, agreeing exactly with the experimental value. *W. D. B.*

A New Method of Determining the Polarization-Capacity. *C. M. Gordon. Zeit. Elektrochemie.* **3**, *163* (*1896*). The electrodes to be measured are balanced against a condenser by means of a Wheatstone's bridge, the telephone being used to determine the zero point. When the cell to be examined has an electromotive force of its own a second condenser is placed next the telephone. *W. D. B.*

Electrolysis and Electrolytic Dissociation

On the Passage of Electricity through Gases exposed to Röntgen Rays. *J. J. Thomson and E. Rutherford. Phil. Mag.* [*5*], **42**, *392* (*1896*). Upon exposure to X-rays gases acquire electrical conductivity. Experiments show that this conductivity does not vanish immediately when the exposure ceases. Passage through a white hot porcelain tube does not destroy the conductivity but passage through water or through a plug of glass wool does. Fine wire gauze or muslin has no effect. Passing an electric current through the gas destroys its conductivity. Molecular-kinetic considerations lead to the conclusion that for air the charged particles have a velocity of about 0.33 cm. sec^{-1} for a gradient of 1 volt. cm^{-1}. Experiment failed to show polarization of the electrodes due to the passage of a current. For the experimental details we must refer to the original paper. *E. B.*

On the Affinity Constants of Organic Acids. *B. Schischkofsky. Jour. Russ. Soc.* **28**, *I*, *604* (*1896*). The author attempts to establish relations among the affinity constants of secondary and tertiary oxyacids and the structure formulas after the usual method and with the usual result. *E. St.*

On the Peroxy-nitrate of Silver. *E. Mulder and J. Heringa. Recueil Trav. Pays-Bas.* **15**, *1* (*1896*). A black, crystalline body, which is formed in small quantity at the anode of a silver voltameter during electrolysis, is made the object of a chemical study. The empirical formula $3Ag_2O.5O.AgNO_3$ is found. The yield varies with the current, temperature and other conditions. The substance tends to decompose spontaneously, notably above 90°C; the conditions giving maximum yield seem to correspond to a minimum velocity of decomposition. The substance can be decomposed in such wise that the needles in which it appears are replaced by their skeletons in silver. The investigation is to be continued. *J. E. T.*

The Platinizing of Electrodes for Telephonic Determination of the Resistances of Liquids. *F. Kohlrausch. Verh. phys. Ges. Berlin,* **15**, *126* (*1896*). The electrolytic platinizing of electrodes with the solution of Lummer and Kurlbaum gives so admirable results that the determination of resistances can be simplified by placing the liquids in U-shaped tubes and either bringing the electrodes to certain marks between which the resistance capacity is known, or, yet more simply, by displacing one of the electrodes along a scale calibrated for resistances. *J. E. T.*

On the Diazotizing of Anilin. *S. Niementowski and J. Roskowski. Bull. Acad. Cracovie,* **1896**, *324*. The authors have furnished data for the solubilities and electrical conductivities of the nitrites of sodium, potassium and silver, and the sulfate and hydrochlorid of anilin, and they have studied the reaction between these nitrites and aqueous anilin, the neutral aqueous anilin salts, and the latter strongly acidified.' In the first two cases the product is diazoamidobenzene

$$2C_6H_5NH_2 + AgNO_2 = 2H_2O + (C_6H_5)N_3Ag$$

but in the acid solutions the salts of diazobenzene form the chief product. It was found that the yield is proportional to the degree of dilution, and that under otherwise like conditions the chemical system with the highest reaction velocity is made up of constituents having equal electrolytic dissociation. *J. E. T.*

Corrections for my Article: Experimental Researches on the Electrolysis of Water. *A. P. Sokolow. Wied. Ann.* **59**, *802* (*1896*). Three pages of corrections of numerical errors in the paper reviewed in this Journal, **1**, *125*. *J. E. T.*

On the Specific Gravity and Electrical Conductivity of the Normal Solutions of Sodium and Potassium Hydroxids, and

Hydrochloric, Sulphuric, Nitric and Oxalic Acids. *E. H. Loomis. Phys. Rev.* 4, *152* (*1896*). The specific gravities were referred to that of water at 4°, the conductivities to that of mercury at 4°. The results are:

NaOH	sp. gr. 1.0418;	$K.10^7$ 145	HNO_3	sp. gr. 1.0324;	$K.10^7$ 278
KOH	1.0481	170	H_2SO_4	1.0306	183
HCl	1.0165	279	$(COOH)_2$	1.0199	55

J. E. T.

On the Electrolytic Condition of Solutions in Methyl Alcohol. *N. Zelinsky and S. Krapiwin. Jour. Russ. Soc.* **28**, *579; Zeit. phys. Chem.* **21**, *35* (*1896*). Measurements at 25°C, of the electrical conductivity of solutions of twenty substances—organic and inorganic salts and acids—in carefully dried methyl alcohol; and of some of them in water and in various mixtures of water and methyl alcohol. The concentrations in most cases were one mol. wt. in grams in 16 to 1024 liters.

The molecular conductivities in methyl alcohol of the bromids and iodids of potassium and ammonium come within thirty per cent of those in water; the haloid salts of the tetra-substituted ammonias and of the tri-substituted sulfins conduct almost as well in methyl alcohol as in water; while the conductivity of ethyl-menthylamin nitrate is *greater* in alcoholic than in aqueous solution. Methyl alcohol solutions of oxalic and of iodic acids on the other hand are very poor electrolytes.

Addition of water to the alcoholic solutions generally reduces the molecular conductivity. To such an extent is this the case that the conductivities of solutions of the bromids and iodids of potassium and ammonium in a mixture of equal parts of methyl alcohol and water is actually less than that of their solution in pure methyl alcohol.

Ostwald's formula connecting conductivity and dilution is in accordance with the measurements made on solutions of stannethyl iodid $SnEt_2I_2$, and of trichloracetic acid, in methyl alcohol.

W. L. M.

On the Electrolytic Dissociation of Certain Acids at Different Temperatures. *H. Euler. Zeit. phys. Chem.* **21**, *257* (*1896*). A continuation of the work of E. Schroeder, Zeit. phys. Chem. **16**, 72 (1895); like the latter it goes to show that the increase in conductivity of solutions which generally accompanies a rise in their temperature is for the most part not dependent on an increase in the dissociation, but must rather be ascribed to a diminution of frictional resistance to the movement of the ions.

The author has measured the electrical conductivity of *n*/50 to *n*/1000 solutions of benzoic, *o*-toluylic, salicylic, *m*-oxybenzoic, *m*- and *o*-nitrobenzoic and dichloracetic acids, at 0°*C* and at temperatures from 20°*C* to 50°*C* at intervals of five degrees; to provide data for determining μ_∞ he has also measured *n*/1000 solutions of the sodium salts of the five acids first named (dichloracetic and *o*-nitrobenzoic acids gave unsatisfactory results). The electrolytic dissociation constants were then calculated and from them the heats of dissociation. The latter in all five cases increase with rise of the temperature; in three cases a change of sign was observed, *viz*: benzoic between 30° and 40°*C*, *m*-oxybenzoic between 20° and 30°*C*, *m*-nitrobenzoic at 50°*C*. *W. L. M.*

On the Electrolysis of Salts and Bases in the Presence of Ammonia. *S. M. Losanitsch and M. Z. Jovitschitsch. Ber. chem. Ges. Berlin* **29**, *2436* (*1896*). If solutions of potassium hydrate, chlorid, bromid, iodid, fluorid, or sulfate be mixed with ammonia and submitted to electrolysis, the volume of the nitrogen given off is always less than one-third that of the hydrogen. The ‹secondary› reactions involved lead to the formation of the nitrite, hypochlorite, *etc.*, of potassium and of the chlorid or iodid of nitrogen; they may be avoided altogether by electrolyzing hot dilute solutions.

W. L. M.

On the Hypothesis of Colored Ions. *G. Magnanini. Gazz. chim. Ital.* **26**, *II, 92* (*1896*). Solid dimethylvioluric acid is colorless; the solutions of the free acid and of the potassium salt are violet. With isonitrosodiketohydrindene the ion is probably reddish while the undissociated substance is yellow. Dichlorquinonemalonic ester is only slightly soluble in water and the solution is faintly blue in color. On adding an alkali the color changes to an intense blue. The salt is quite soluble. *W. D. B.*

The Use of Porous Carbon Cylinders in Electrolytic Experiments. *W. Löb. Zeit. Elektrochemie,* **3,** *185* (*1896*). If a carbon cup filled with copper sulfate solution is made the cathode in electrolyzing sulfuric acid, copper is deposited on the inside of the cylinder and little or no hydrogen is evolved on the outside. If the positions of the two liquids be reversed, copper deposits on the outside of the cup and no hydrogen is given off on the inside. This seems analogous to the experiments of Braun on stenolysis. Hydrogen as ion can pass through carbon while copper can not. *W. D. B.*

Notice upon the Electrolytic Purification of Cadmium. *F. Mylius and R. Funk. Zeit. anorg. Chem.* **13,** *157* (*1896*). By electrolyzing cadmium sulfate and distilling the metal *in vacuo* it is easy to obtain cadmium which contains less than 0.001 per cent of metallic impurities. *W. D. B.*

Critical Studies on the Volumetric Determination of Caustic Alkali containing Carbonates and of Alkaline Carbonates as well as on the Behavior of Phenolphthalein and Methylorange as Indicators. *F. W. Küster. Zeit. anorg. Chem.* **13,** *127* (*1896*). The different methods of titrating caustic alkalies give widely varying results. The errors are due in part to occlusion of the alkali by the precipitate formed and still more to the fact that in dilute solutions, carbonic acid does not act as a monobasic acid towards phenolphthalein and does act as an acid towards methylorange. With methylorange as an indicator it is necessary to titrate to a certain color; with phenolphthalein it is necessary to add a soluble sodium salt if one wishes to obtain accurate results. The author does not accept Ostwald's rather unsatisfactory assumption that the methylorange ion is yellow; but he does not establish his own view. It is much to be desired that the effect of alcohol and acetone upon indicators should receive some attention. *W. D. B.*

On Solutions of Trichloracetic Acid. *P. Rivals. Comptes rendus,* **123,** *240* (*1896*). The author attributes to Ostwald the statement that the change of conductivity with the concentration is a function of the heat of dilution and then shows that this is not true for trichloracetic acid. It would be interesting to know where Ostwald made this statement. *W. D. B.*

A General Method of preparing Sulfids by Electrolysis. *R. Lorenz. Zeit. anorg. Chem.* **12,** *442* (*1896*). The anode is the metal which is to be converted into sulfid, the cathode is a stick of copper sulfid and the electrolyte is a salt of an alkali metal. The author claims that this does away with the use of alkali sulfids; but since these are formed during the electrolysis, the method seems a complete waste of time. *W. D. B.*

A General Method of preparing Hydroxids by Electrolysis. *R. Lorenz. Zeit. anorg. Chem.* **12,** *436* (*1896*). The precipitation of hydroxids by caustic alkali is not convenient owing to the difficulty of washing the precipitate. This may be avoided by electrolyzing any salt of the alkali metals using as anode the metal which one wishes to convert into hydroxid. This method presupposes pure metal as anode. It seems to offer no advantage over acting upon a salt of the metal with caustic potash or soda and neutralizing the excess of alkali. *W. D. B.*

On the Preparation of Potassium Pyrochromate by Electrolysis. *R. Lorenz. Zeit. anorg. Chem.* **12,** *396* (*1896*). Ferrochrome is used as anode in alkaline solution. The iron forms a hydroxid and does not go into solution. *W. D. B.*

On the Preparation of Potassium Permanganate by Electrolysis. *R. Lorenz. Zeit. anorg. Chem.* **12,** *393* (*1896*). By electrolysis of a solution of caustic potash, permanganate of potassium is formed when manganese or an alloy of manganese is used as the anode. *W. D. B.*

Electrolytic Preparation of a New Class of Oxidizing Agents. *E. J. Constam and A. v. Hansen. Zeit. Elektrochemie.* **3,** *137* (*1896*). When a saturated solution of potassium carbonate is electrolyzed at temperatures below − 10° there is formed a bluish white salt, the composition of which is probably represented by the formula $K_2C_2O_6$. This new salt, like hydrogen peroxid, can act either as an oxidizing or a reducing agent. It oxidizes lead sulfid to sulfate while lead peroxid is reduced with evolution of oxygen. With potassium hydrate it gives the carbonate and hydrogen peroxid. *W. D. B.*

On the Electrolysis of the Fatty Acids. *J. Hamonet. Comptes rendus*, **123**, *252* (*1896*). The author finds that the esters formed by the electrolysis of the potassium salts of organic acids decompose in aqueous solution with formation of alcohol and acid. He looks upon this as very remarkable. *W. D. B.*

Method of Desilverizing Lead Electrolytically. *D. Tommasi. Bull. soc. chim. Paris*, **15**, *923* (*1896*). Lead containing silver serves as anode and an aluminum bronze plate as cathode, while the electrolyte is an aqueous solution of the double acetate of lead and potassium. By the action of the current, lead dissolves from the anode and precipitates upon the cathode, while the silver falls to the bottom of the vessel and is removed. The author presents figures to show the commercial advantages of the method. *W. D. B.*

On Several Electrolyzors for Laboratory Use. *P. Fuchs. Zeit. Elektrochemie*, **3**, *223* (*1896*). Two pieces of apparatus for continuous electrolysis. The main features are side tubes for adding and removing the solution and a hard rubber cover giving an airtight joint. In one apparatus the vessel holding the electrolyte is an inverted bell-jar; in the other a beaker set in a wooden stand. *W. D. B.*

On the Conductivity of Electrified Air. *F. Braun. Göttinger Nachrichten*, **1896**, *172*; *Wied. Ann.* **59**, *688* (*1896*). Experiments to show that air free from dust can be electrified. *W. D. B.*

Experiments in Proof of a Directed Surface Conductivity. *F. Braun. Göttinger Nachrichten*, **1896**, *157*; *Wied. Ann.* **59**, *673* (*1896*). The moistened surface of a gypsum plate conducts better in the same direction that the dry crystal does. *W. D. B.*

On the Behavior of Immersed Conductors. *H. Kauffmann. Zeit. Elektrochemie*, **3**, *237* (*1896*). A brief study of the effect of the presence of an isolated metallic conductor in an electrolyte through which a current is passing. If the conductor in question be a sphere filled with an electrolytic fluid, practically no current will flow through the latter. *W. D. B.*

Structure Phenomena

On the Variations in the Crystalline Form of Sodium Chlorid and its Dependence upon the Composition and Properties of the Solutions from which the Salt crystallizes. *P. Orlow. Jour. Russ. Soc.* **28**, *I, 715 (1896).* The author has crystallized salt from very different solutions, paying great attention to the purity of the chemicals and to the temperature and concentration at which the crystallization occurs. He succeeded in obtaining octahedral crystals and truncated cubes more often than Retgers and others have done, as from NaOH and HCl solutions or after addition of some chlorids and sodium salts to neutral solutions. The author is inclined to refer the phenomena to the hydrates and double salts which he assumes to exist in the solution.

The theories of Gibbs and of Curie are not used, though it is mentioned that the capillarity constants must stand in some relation to the properties of the solutions. *E. St.*

Absorption of the Ultraviolet Rays by Crystals and Polychroismus in the Ultraviolet Part of the Spectrum. *Agafonow. Jour. Russ. Soc.* **28**, *II, 200 (1896).* A preliminary notice in which the absorption phenomena are described for one hundred different crystals. The substances which let the ultraviolet rays through are those which crystallize well, and *vice-versa;* see A. Cornu, Comptes rendus, **123**, 490 (1896). With hemimellitic acid and some tourmalines the absorption changed with the relative position of the crystal to the ray. *E. St.*

On Color Photography by the Interferential Method. *G. Lippmann. Proc. Royal Institution, April 17; Proc. Roy. Soc.* **60**, *10 (1896).* Colored photographs are taken by exposing any transparent photographic film with a metallic mirror, as of mercury, behind it, and then developing and fixing as usual. Films are usually opaque, but the precipitation of such compounds as silver bromid does not occur in the presence of an organic colloid, the compounds being formed but remaining invisible, so one has merely to prepare films in the usual way but with a greater proportion of the organic substratum. Gelatinous solutions of $AgNO_3$ and KBr, for example, can be mixed without precipitation, giving transparent films containing up to thirty percent of AgBr.

When a ray of definite wave length falls on the plate it is turned back by the mirror and so produces a set of standing waves in the film, giving rise to a corresponding periodical structure there; this structure then reflects the color which has produced it. The lecturer projected on the screen photographs of various colored subjects; even a portrait from life, exhibiting the delicate hue of the human complexion. His interference theory accords with the facts that the colors are seen only in the direction of specular reflection; that they change with incidence, passing towards the violet; and that they change towards the red if the plate be wetted, the gelatine then swelling. The pictures can not be retouched or falsified.

J. E. T.

Refractometric Investigations. *J. F. Eyckman. Recueil Trav. Pays-Bas*, **15**, *52* (*1896*). Determinations of the refractive indices and of the molecular refractions, calculated by the formula $\frac{n_2 - 1}{n + 0.4}$ *VM*, for a series of paraffin hydrocarbons with 17 to 23 combining weights of carbon. It is concluded that «for the liquid state the refractions and dispersions of homology in the paraffin series are constant, at least from the sixth term on and probably from the third». *J. E. T.*

The Change of Rotation in the Transformation of Lactones into the Corresponding Acids. *W. A. van Ekenstein, W. P. Jorissen and L. T. Reicher. Zeit. phys. Chem.* **21**, *383* (*1896*). The authors make new measurements to complete a table given in van 't Hoff's *Lagerung der Atome im Raume*, *109*, of such rotations. The sodium, potassium, calcium or cadmium salts and the lactones of a number of optically active acids were investigated, and the molecular rotations of their anions and of the corresponding lactones were calculated. *J. E. T.*

The Relation between the Refraction of the Elements and their Chemical Equivalents. *J. H. Gladstone. Proc. Roy. Soc.* **60**, *140* (*1896*). The author arrives at an approximative law,—that the product of the specific refraction of a metal into the square root of its equivalent weight is a constant. The ‹law› does not hold for non-metals. *J. E. T.*

On the Unknown Lines observed in the Spectra of Certain Minerals. *J. N. Lockyer. Proc. Roy. Soc.* **60**, *133* (*1896*). Tabulated wave lengths of unknown lines for the gases obtained from some dozen minerals by the distillation method. *J. E. T.*

On the Spectrum of Cyanogen as produced and modified by Spark Discharges. *W. M. Hartley. Proc. Roy. Soc.* **60**, *216* (*1896*). Discussion accompanying report on experiments to show that with the spark the cyanogen spectrum is far less strongly marked than with a flame of the gas; the spectrum in the latter case is ascribed to the incandescence of an excess of the gas. *J. E. T.*

A Further Study of the Effect of Pressure on the Wave-lengths of Lines in the Arc Spectra of Certain Elements. *W. J. Humphreys. Astrophys. Jour.* **4**, *249* (*1896*). Experiments with forty-six elements show the wave lengths of the lines in their arc spectra to increase with rising pressure, the increase in either half of a Mendelejew group being proportional to the cube roots of the atomic weights of the (metallic) elements. The lines of a few elements, La, Al, Cr, Fe, Ni, shift just one-half the calculated amount. The author suggest a molecular-kinetic explanation of the phenomena. *J. E. T.*

Contributions to the Isomorphism of the Alkali Salts. *R. Krickmeyer. Zeit. phys. Chem.* **21**, *53*, (*1896*). The method of investigation consisted in crystallizing solutions of salts containing K, NH_4, Na, Li, and determining from the specific gravity of the crystals, checked by analysis, whether the crystals were homogeneous crystalline mixtures of varying composition, *Mischkrystalle*, or crystals of fixed composition. When, on varying the proportions of salts, homogeneous crystalline mixtures of varying composition could be obtained the metals, including NH_4, were considered strictly isomorphous; a failure to produce homogeneous crystalline mixtures indicated incomplete isomorphism or its total absence. Homogeneous crystalline mixtures were obtained with :—

Potassium alum with ammonium alum ;

$K_2SO_4.MSO_4.6aq$ with $(NH_4)_2SO_4.MSO_4.6aq$, where M = Zn, Ni, Co ;

KCl with NH_4Cl ;

KH_2PO_4 with $NH_4H_2PO_4$;

Homogeneous crystalline mixtures could not be obtained with :—

$K_2C_4H_4O_6.\frac{1}{2}H_2O$ with $NH_4C_4H_4O_6$; probably on account of the water of crystallization ;

Sodium alum with potassium alum ; NaCl with KCl ;

$Na_2SO_4.ZnSO_4.4aq$ with $K_2SO_4.ZnSO_46aq$;

$NaBr.2H_2O$ with KBr ;

Sodium alum with ammonium alum ;

NaCl with NH_4Cl ; LiCl with NaCl ;

$Li_2SO_4.H_2O$ with Na_2SO_4 ; $Li_2SO_4.H_2O$ with K_2SO_4 ;

$LiNO_3$ with $NaNO_3$; LiCl with KCl ;

Hence, K and NH_4 are strictly isomorphous, while neither K, Na, Li, nor NH_4, Na, are so. A comparison of Li with NH_4 was not made.

C. L. S.

On the Crystallographic Relations of Optically Active Substances. *H. Traube. Ber. chem. Ges. Berlin*, **29**, *2447* (*1896*). In the majority of cases goniometric measurements alone are insufficient to determine the crystallographic system to which a given substance belongs. As an illustration, a crystal presenting a six sided prism and base may be a member of any one of twelve different groups ; and optical, pyroelectrical or other physical measurements are necessary to a more precise definition.

Under this head come all the exceptions quoted by Walden [Ber. **29**, 1692 (1896) ; this Journal **1**, 115] to Pasteur's law, that all substances which in solution are optically active crystallize in hemihedral forms. In no case in which a complete crystallographic examination has been made, has an exception to the law just quoted been discovered.

W. L. M.

On the Power of Rotation of Optically Active Crystals when finely Divided. *H. Landolt. Ber. chem. Ges. Berlin*, **29**, *2404* (*1896*). The power of optical rotation possessed by the (cubical) crystals of sodium chlorate remains unaltered when the crystals are powdered as finely as possible, (diam. of the particles 0.004 mm), and suspended in a mixture of alcohol and carbon disulfide with the same refractive index as themselves.

Solutions of the salt in question are optically inactive; the author finds the same to be true for «solutions from which crystals have just been deposited, and for supersaturated solutions, in which possibly larger molecular aggregations may occur»—this result is in accordance with all that is known on the subject of saturation.

In connection with this research, Landolt describes an ingenious method of Quincke's for determining the average diameter of the particles of a fine powder; this is based on the fact that if a glass plate be uniformly dusted over with the powder, and held between the eye and a small sodium flame, the latter appears surrounded with an aureole whose diameter depends on the size of the particles composing the powder. *W. L. M.*

On Magnetic Rotary Power, especially of Aromatic Compounds. *Zeit. phys. Chem.* **21**, *451* (*1896*). Reprinted from the *Jour. Chem. Soc.* and reviewed in this Journal **1**, 191.

On the Transparency of Substances for X-rays. *E. van Aubel. Jour. de Phys.* (*3*) **5**, *511* (*1896*). The author cites instances to show that substances readily permeable to heat rays are opaque towards X-rays and *vice versa.* *W. D. B.*

On the Absorption of the Ultraviolet Spectrum by Crystallin Substances. *A. Cornu. Comptes rendus*, **123**, *490* (1896). There is a strong analogy between the absorption by the crystals and by the same substances in solution. The sulfates are very transparent, the nitrates show marked absorption of the ultraviolet rays while the chromates cut off the ultraviolet and blue of the spectrum. Many organic substances absorb the whole of the ultraviolet. The author hints at a relation between transparency and the power of forming large crystals. This is probably only an accidental coincidence.

W. D. B.

Contributions to the Knowledge of Isomorphism. *XII. J. W. Retgers. Zeit. phys. Chem.* **20**, *481* (*1896*). The first section of the paper is devoted to proving that beryllium is not isomorphous with the metals of the magnesium group. The second part is nominally about the figures obtained by etching and their importance in determining questions of isomorphism; but, in reality, it is far more than that and is a partial review of the whole subject of isomorphism together with an outline of the work to be done and the way in which it should be done. In the third section the question of abnormal mixtures is taken up. Under abnormal mixtures are understood crystals which have been colored with organic dye-stuffs. Attention is called to the fact that such crystals often have a fibrous structure and this suggests the possibility that the occurrence of fibrous quarz and even of asbestos is due chiefly to the nature of the other substances in the original solution.

This paper has a melancholy interest attaching to it, being the last article written by the author. Jan Willem Retgers had spent scant eight years in the study of isomorphism; but in that time he accomplished a wonderful amount of work in spite of continued ill-health. A careful study of his papers will repay the student a hundred fold. *W. D. B.*

Corrosion Phenomena with Zinc Plates. *F. Mylius and R. Funk. Zeit. anorg. Chem.* **13**, *151* (*1896*). A brief notice of changes in surface produced by oils or by hammering. The phenomena are very surprising and are well worthy of further study. *W. D. B.*

On the Transparency of Solutions of Colorless Salts. *W. Spring. Zeit. anorg. Chem.* **13**, *19* (*1896*). The presence of lithium, sodium, potassium, magnesium, strontium, calcium and barium chlorids; of potassium bromid; and of sodium and potassium nitrates has no effect upon the color of a layer of water, twenty-six meters thick. Light is absorbed by these solutions but the amount is not strictly proportional to the concentration. It is probable that the absorption is a function of the electrolytic dissociation. The author suggests that the transparency of metals may be a function of the conductivity. *W. D. B.*

The Rôle of the Röntgen Rays in Chemistry. *A. v. Hemptinne. Zeit. phys. Chem.* **21**, *493* (*1896*). The X-rays have no effect upon the conductivity of solutions nor upon the rate of saponification of esters and do not cause mixtures of chlorin and hydrogen or of chlorin and carbon monoxid to explode. *W. D. B.*

On the Relations between the Viscosity (Internal Friction) of Liquids and their Chemical Nature. *Part II. T. E. Thorpe and J. W. Rodger. Proc. Roy. Soc.* **60,** *152* (*1896*). The viscosities of ten esters and five ethers were determined. In no case was there any evidence of polymerization. *W. D. B.*

The Permeability of Various Elements to the Röntgen Rays. *J. Waddell. Chem. News.* **74,** *298* (*1896*). No important results were obtained. *W. D. B.*

On the Symmetrical Relations in Crystals. *V. v. Lang. Zeit. phys. Chem.* **21,** *218* (*1896*). The author gives a short proof that there are exactly thirty-two kinds of symmetry possible in crystals. The conclusion is generally accepted and the object of the paper seems to be to call attention to the soundness of the author's point of view as expressed in his text book of thirty years ago.

W. D. B.

On the Structure of Metals, *its Origin and Changes. F. Osmond. and W. Roberts Austen. Proc. Roy. Soc.* **60,** *148* (*1896*). The authors made a microscopical examination of gold alloyed with 0.2 per cent of various elements. They conclude that there is no relation between either the structure, the appearance of the fractures, the melting points of the alloyed elements and the mechanical properties of the masses of alloyed gold. When gold alloyed with bismuth, thallium, antimony or aluminum is annealed in sulfuric acid at about 250° the large grains of the metal become divided into a multitude of little polyhedral grains. *W. D. B.*

On Various Properties of Uranium Rays. *H. Becquerel. Comtes rendus,* **123,** *855* (*1896*). Uranium and salts of uranium emit photographically active rays even after having been kept in the dark for eight months. These rays, like the Röntgen rays, discharge electrified bodies. *W. D. B.*

ON QUINTUPLE POINTS

BY WILDER D. BANCROFT

In a system composed of two salts and water there will be in equilibrium at the quintuple points, three solid phases, solution and vapor. All nonvariant systems, save one, if kept at constant pressure, will change on addition of heat from three solid phases into two pairs of solid phases and solution or into one pair of solid phases and solution. With certain limitations—to be defined later—the inversion point will be, in the first case, a minimum temperature for one of the solid phases in equilibrium with solution and vapor; in the second case, a maximum temperature for some solid phase under the same conditions.[1] In all cases there is disappearance of one or more solid phases and formation of solution. This is in accordance with the theorem of Le Chatelier that addition of heat causes an increase in the system which is formed with the absorption of heat. Keeping this in mind it is possible, in many cases, to tell which solid phase can exist in equilibrium with solution and vapor only above or below the quintuple point and whether it is above or below.

The various quintuple points can be classified under three heads.

I. Two of the solid phases can be made from the third with addition or subtraction of water.

II. One of the solid phases can be transformed into one of the others by addition or subtraction of water.

III. No one of the solid phases can be converted into either of the others by addition or subtraction of water.

For quintuple points of the first type the following rule holds in all the instances yet studied. When one of the solid phases can change into the other two with the addition or subtraction of water, the inversion point is a minimum temperature for that phase if the

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[1] If these conditions are not insisted upon the only general statement possible in respect to a hydrated double salt has already been made by Roozeboom. Zeit. phys. Chem. 2, 517 (1897).

water be added to complete the reaction and a maximum temperature if the water be subtracted. The following instances will illustrate this rule. At −3° one of the double sulfates of magnesium and potassium changes into the single sulfates with addition of water.[1] This is, therefore, a minimum temperature for $K_2Mg(SO_4)6H_2O$.

$$K_2Mg(SO_4)_26H_2O + H_2O \rightleftarrows K_2SO_4 + MgSO_47H_2O.$$

The same change takes place at 21.5° with the double sulfate of sodium and magnesium.[2] This is a minimum temperature for $Na_2Mg(SO_4)_24H_2O$.

$$Na_2Mg(SO_4)_24H_2O + 13H_2O \rightleftarrows Na_2SO_410H_2O + MgSO_47H_2O.$$

Copper potassium chlorid changes at 56° into copper potassium chlorid and hydrated cupric chlorid.[3] This is a minimum temperature for $CuCl_2KCl$.

$$2CuCl_2KCl + 4H_2O \rightleftarrows CuCl_22KCl2H_2O + CuCl_22H_2O$$

At 92° copper dipotassium chlorid changes into copper potassium chlorid.[3] This is a maximum temperature for $CuCl_22KCl2H_2O$.

$$CuCl_22KCl2H_2O - 2H_2O \rightleftarrows CuCl_2KCl + KCl$$

An analogous change occurs at 146° with copper diammonium chlorid.[4] This is a maximum temperature for $CuCl_22NH_4Cl2HO$.

$$CuCl_22NH_4Cl2H_2O - 2H_2O \rightleftarrows CuCl_2NH_4Cl + NH_4Cl.$$

At 15.5° one of the double salts of copper and tetrethylammonium chlorids changes into another double salt and hydrated cupric chlorid.[5] This is a minimum temperature for $(CuCl_2)_52N(C_2H_5)_4Cl$.

$$(CuCl_2)_52N(C_2H_5)_4Cl + 8H_2O \rightleftarrows CuCl_22N(C_2H_5)_4Cl + 4CuCl_22H_2O.$$

The double salt of copper and calcium acetates changes at 76° into the single acetates.[6] This is a maximum temperature for $CuCaAc_48H_2O$.

$$CuCaAc_48H_2O - 6H_2O \rightleftarrows CuAc_2H_2O + CaAc_2H_2O.$$

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[1] van der Heide. Zeit. phys. Chem. **12**, 416 (1893).

[2] van 't Hoff and van Deventer. Ibid. **1**, 165 (1887).

[3] Meyerhoffer. Ibid. **3**, 336 (1889).

[4] Meyerhoffer. Ibid. **5**, 98 (1890).

[5] Meyerhoffer. Sitzungsber. Akad. Wiss. Wien, **102**, IIb 150 (1893).

[6] Reicher. Zeit. phys. Chem. **1**, 221 (1887).

The double sodium ammonium racemate decomposes at 27° into the dextrorotary and laevorotary sodium ammonium tartrates.[1] This is a minimum temperature for $(NaNH_4C_4H_4O_6H_2O)_2$.

$$(NaNH_4C_4H_4O_6H_2O)_2 + 6H_2O \rightleftarrows 2(NaNH_4C_4H_4O_64H_2O).$$

This same salt changes at 35° into the single racemates.[2] This is a maximum temperature for $(NaNH_4C_4H_4O_6H_2O)_2$.

$$2(NaNH_4C_4H_4O_6H_2O)_2 - 4H_2O \rightleftarrows (Na_2C_4H_4O_6)_2 + ([NH_4]_2C_4H_4O_6)_2.$$

The same changes take place with the double potassium sodium racemate at the temperatures of — 6° and 41° respectively[3] the first being a minimum and the second a maximum temperature for $(KNaC_4H_4O_63H_2O)_2$.

$$(KNaC_4H_4O_63H_2O)_2 + 2H_2O \rightleftarrows 2(KNaC_4H_4O_64H_2O)$$

$$2(KNaC_4H_4O_63H_2O)_2 - 8H_2O \rightleftarrows (Na_2C_4H_4O_6)_2 + (K_2C_4H_4O_62H_2O_2).$$

For quintuple points of the second type the following rule may be stated: If one solid phase can be converted into one of the others by addition of water the inversion point is a maximum or a minimum temperature for one of those phases and is neither a maximum nor a minimum for the third solid phase. This can be illustrated very readily by three instances from the system, potassium sulfate, magnesium sulfate and water. At 47.2° two of the phases are $MgSO_47H_2O$ and $MgSO_46H_2O$, the third is $K_2Mg(SO_4)_26H_2O$. This is a minimum temperature for the hexahydrate. The hydrated double salt exists both above and below the temperature of the inversion point. At 72° two of the solid phases are the hydrated double salts $K_2Mg(SO_4)_26H_2O$ and $K_2Mg(SO_4)_24H_2O$ while the third is magnesium sulfate heptahydrate. At 92° two of the solid phases are the same two hydrated double salts and the third is potassium sulfate. The first temperature is a minimum for the double salt with four units of water and the second a maximum for the one with six of water. If the temperatures are not given it can only be told by experiment which point is which. If the compositions of the

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[1] van 't Hoff and van Deventer. Zeit. phys. Chem. **1**, 165 (1887)
[2] van 't Hoff, Goldschmidt and Jorissen. Ibid. **17**, 49 (1895).
[3] van 't Hoff and Goldschmidt. Ibid. **17**, 505 (1895).

solutions are known, the direction of the temperature change can be foretold from the theorem of van Alkemade[1] that the temperature rises along the boundary curve in the direction of the line connecting the melting points of the two solid phases. The higher temperature will necessarily be a maximum for the double salt with a larger amount of water of crystallization.

It may not be clear why there is an uncertainty for quintuple points of the second type and not for those of the first type. For these latter the equation shows that the double salt can not exist above the inversion temperature in equilibrium with solution and vapor nor the two single salts below it. This necessitates that the two monovariant systems with double salt and one component, double salt and the other component as solid phases, must exist at temperatures below that of the quintuple point and thus there is complete information, so far as temperature is concerned, in regard to the three solubility curves. With quintuple points of the second type the equation shows the temperature change for two of the curves but gives no information in regard to the third, along which the solid phases are the two compounds entering into the equation.

When no one of the three solid phases can be converted into either of the others, it is impossible to make any definite prediction if the only data are the formulas of the three solid phases. As an instance, let us take the two quintuple points where the solid phases are ice, hydrated calcium acetate and copper calcium acetate; ice, hydrated copper acetate and copper calcium acetate. The two sets consist of ice, a hydrated salt and a hydrated double salt. There is no way of distinguishing them without further information. Here again the theorem of van Alkemade will help us if the concentrations of the two solutions are known and if the double salt is decomposed by water. This has been expressed in the following form by Schreinemakers:[2] «The cryohydric temperature of a solution in equilibrium with double salt and the component which does not precipitate is lower than the cryohydric temperature of the solution in equilibrium with double salt and the component which does precipitate ».

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[1] Zeit. phys. Chem. **11**, 289 (1893).
[2] Ibid. **12**, 851 (1893).

If the double salt is stable in the presence of water, there is no *a priori* method of telling which cryohydric temperature is the higher. It should be clearly understood that in all these cases a maximum or a minimum temperature for a given substance refers to that solid phase in equilibrium with solution and vapor. For instance, 56° is a minimum temperature for copper potassium chlorid in equilibrium with solution and vapor; but it is possible for copper dipotassium chlorid, copper potassium chlorid, potassium chlorid and vapor to be in stable equilibrium at room temperature.

When an anhydrous and a hydrated double salt combine to form a hydrated double salt with addition or subtraction of water, there seems, at first, no reason why there should not be a quintuple point at which these three solid phases could be in equilibrium with solution and vapor, yet this is not possible. To take a concrete case let us assume that lead and potassium iodids form no anhydrous double salt and only one hydrated double salt, PbI_2KI2H_2O. If the nonvariant system, hydrated lead iodid, potassium iodid, lead potassium iodid, solution and vapor, can exist it will be possible to have these three salts in equilibrium with vapor over a series of temperatures. A moment's consideration will show that there is no way in which this system can effloresce without forming a new solid phase and thus a nonvariant system capable of existing over an indefinite range of temperature. Since this is impossible, it follows that a quintuple point with these three salts as solid phases can not exist and that another solid phase must appear before this point is reached. Under the conditions assumed to exist, the new phase would be lead iodid, either anhydrous or with one of water. As a matter of fact, it is probable that lead and potassium iodids form a second hydrated double salt and it is this phase which appears.[1] The hydrated double chlorid of copper and potassium can be made from potassium chlorid and hydrated cupric chlorid without addition or subtraction of water. Here it is known that the anhydrous double salt, $CuCl_2KCl$, appears as solid phase and that copper dipotassium chlorid, potassium chlorid and hydrated cupric chlorid can not coexist in equilibrium with solution and vapor. There is a sugges-

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[1] Schreinemakers. Zeit. phys. Chem. **10**, 471 (1892).

tion of this relation in a paper by Schreinemakers[1] in which he implies that there can not be two hydrated double salts at the quintuple point with the same amount of water of crystallization ; but he offers no proof for this, limits it to hydrated double salts and does not take into account the third solid phase. In his paper on lead and potassium iodids he sees no theoretical impossibility in there being a temperature at which the hydrated double salt might change into its components.[2]

These applications of the theorem of Le Chatelier may sometimes be useful in throwing light on the possible constitution of a solid phase. Schreinemakers thinks that at 190° hydrated lead iodid $PbI_2 2H_2O$, and lead potassium iodide, PbI_2KI2H_2O, are in equilibrium with solution, vapor and a second hydrated double salt. When potassium iodid is substituted for hydrated lead iodid, the resulting nonvariant system is supposed to exist at 170°. Assuming that these two temperatures are approximately correct and that the unknown phase is the same in both cases with the formula, $PbI_2 xKI yH_2O$, it is clear that 170° is the lowest temperature at which the new double salt can exist in equilibrium with solution and vapor and that 190° is the highest temperature possible for the ordinary double salt under the same conditions. The two equations expressing these facts are :

$$PbI_2 xKI yH_2O + (2-y)H_2O \rightleftarrows PbI_2KI2H_2O + (x-1)KI \text{ at } 170^\circ$$

$$x(PbI_2KI2H_2O) - (2-y)H_2O \rightleftarrows$$
$$(x-1)PbI_2 2H_2O + PbI_2 xKI yH_2O \text{ at } 190^\circ.$$

In order that there shall be no negative quantities and that there shall be three solid phases at 170° we see that y must be less than two and may be zero while x can not be less than unity nor equal to infinity. Since x cannot equal zero it follows that the new phase is neither anhydrous nor monohydrated lead iodid and is a double salt.

If $x = 1$ the two equations become indeterminate. Since the hydrated double salt, PbI_2KI2H_2O, is always decomposed by water with precipitation of hydrated lead iodid, the theorem of van Alke-

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[1] Zeit. phys. Chem. **11**, 941 (1893).

[2] Ibid. **10**, 476 (1892).

made requires that the quintuple point with hydrated lead iodid as solid phase should occur at a higher temperature than the quintuple point with potassium iodid as solid phase. Since 190° is higher than 170° the change may be one of dehydration only. We can therefore draw the following conclusions: The new solid phase must be a double salt; it must contain less than two units of crystal water and may be anhydrous; the ratio of potassium to lead can not be less than unity nor equal to infinity. It must be remembered that these conclusions rest upon the assumption that the same solid phase appears at the two quintuple points.

The results of this paper may be assumed as follows:

1. When one of the solid phases can change into the other two with addition or subtraction of water, the inversion point is a minimum temperature for that phase if the water be added to complete the reaction and a maximum if the water be subtracted.

2. If one of the solid phases can be converted into one of the others by addition of water, the inversion point is a maximum or a minimum temperature for one of those phases and is neither a maximum nor a minimum for the third solid phase.

3. When no one of the solid phases can be converted into either of the others by addition or subtraction of water no prediction can be made.

4. There can not be in equilibrium three solid phases such that one can be made from the other two without addion or subtraction of water.

5. If the same solid phase appears at 170° and 190° in the system, lead iodid, potassium iodid and water, it must be a double salt and the ratio of potassium to lead may exceed unity.

Cornell University, September 1896.

SOLIDS AND VAPORS

SECOND PAPER

BY WILDER D. BANCROFT

While many salts in efflorescing at constant temperature form all intermediate hydrates, it is well known that this is not always the case. To take a single example, sodium sulfate with ten of water changes normally to the anhydrous salt without formation of the salt with seven of water. Phenomena of this sort can always be made plausible by elaborating structure formulas which describe the facts, and the success of this method in organic chemistry prompts many to undertake the same task for inorganic chemistry. The facts can be stated with equal accuracy for hydrated salts, both single and double, without any reference to a hypothetical molecular structure. If we start with hydrated sodium sulfate, solution and vapor, and raise the temperature to about 33° there will be formed anhydrous sodium sulfate. On decreasing the external pressure the solution will disappear, leaving the stable monovariant system, hydrated and anhydrous sodium sulfate, and vapor. Decreasing the pressure yet more, the salt with ten of water must effloresce with formation of the anhydrous salt. Were it to form the salt with seven of water there would be present a nonvariant system. This would also be formed from the monovariant system at any other temperature at which the latter could exist and we should have the phenomenon of a nonvariant system existing at a series of temperatures and pressures, a state of things which is impossible according to the Phase Rule.

We may therefore state the general rule as follows: A hydrated salt effloresces normally with formation of the solid phase which can coexist at the next higher quadruple point. If all the known hydrates of a salt can exist in stable equilibrium with solution and vapor at some temperature, all the lower hydrates will be formed successively when a given hydrate effloresces normally. This does not exclude the possibility of sometimes skipping some hydrate.

Roozeboom[1] found that it was easy to pass from ferric chlorid with twelve of water in presence of solution and vapor to the salt with five of water without the salt with seven of water being formed at all. This can also happen with efflorescing salts and Lescoeur[2] found in his experiments that the salt with twelve of water effloresced without formation of the salt with seven. The system thus formed was instable and would have changed if a crystal of the latter salt had been added. It is also probable that sodium sulfate with ten of water would effloresce to the salt with seven of water if a crystal of the latter were added, though this has not been tried to my knowledge. This last is not quite parallel to the behavior of ferric chlorid because it is probable that the system, sodium sulfate with ten of water, sodium sulfate heptahydrate and vapor, is stable in respect to the anhydrous salt.

It is also possible to predict the behavior of hydrated double salts under different conditions. Assuming that the pressure temperature curves for the monovariant systems composed of three solid phases and vapor do not intersect, we have the general rule describing the normal efflorescence of all ternary systems in which only one component is measurably volatile at the temperature of the experiment: Two solid phases containing three components will effloresce with formation of the solid phase which can exist in equilibrium with them at the next higher quintuple point. A few illustrations will show the predictions which one can make on the strength of this rule and will exemplify the apparent irregularity of the phenomena. One might expect that when the two solid phases are a hydrated salt and a hydrated double salt, one or the other would always effloresce first regardless of the nature of the components; but this is not true.

The double acetate of copper and calcium $CuCaAc_4 8H_2O$, taken by itself or in presence of either of the components, effloresces with formation of the two single salts as predicted.[3] Here the hydrated double salt effloresces before either of the single salts, the change

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[1] Zeit. phys. Chem. **10**, 493 (1892).
[2] Ann. chim. phys. (7) **2**, 93 (1894).
[3] Reicher. Zeit. phys. Chem. **1**, 221 (1887).

and the pressure at which it takes place being independent of the nature of the second solid phase. With the double chlorid of copper and potassium the hydrated double salt always effloresces when the external pressure is decreased but the nature of the change and the pressure at which it takes place are dependent on the second solid phase.[1] Starting from the system $CuCl_2 2KCl 2H_2O$, $CuCl_2 2H_2O$, $CuCl_2 KCl$ and vapor, and decreasing the external pressure, there will be disappearance of copper dipotassium chlorid and hydrated copper chlorid with formation of copper potassium chlorid. If the hydrated double salt be present in excess, hydrated copper chlorid will be the first phase to disappear, forming the divariant system, $CuCl_2 2KCl 2H_2O$, $Cl_2 KCl$ and vapor. At a yet lower pressure the hydrated double salt will effloresce with formation of potassium chlorid and copper potassium chlorid, the pressure remaining constant so long as the monovariant system, $CuCl_2 2KCl 2H_2O$, KCl, $CuCl_2 KCl$ and vapor is present. If hydrated copper chlorid were originally in excess instead of hydrated double salt, this latter would be the first to disappear, leaving the divariant system, $CuCl_2 2H_2O$, $CuCl_2 KCl$ and vapor. This will remain in stable equilibrium until the pressure falls below the value for the system, $CuCl_2 2H_2O$, $CuCl_2$, $CuCl_2 KCl$ and vapor. If we start with the hydrated double salt, alone or in presence of either or both of the salts, KCl and $CuCl_2 KCl$, the hydrated double salt will effloresce with formation of potassium chlorid and copper potassium chlorid. It will be noticed that the reactions and the pressures at which they take place are functions of the nature and relative amounts of the solid phases originally present and that these changes are all in accordance with the general rule.

The hydrated double salt is not necessarily the first solid phase to effloresce. While there are no experimental data as yet, it seems fairly certain that a mixture of magnesium sulfate heptahydrate and sodium sulfate decahydrate will effloresce with formation of the hydrated double salt, $Na_2Mg(SO_4)_2 4H_2O$. If the sodium salt is present in excess, this will then effloresce forming the anhydrous salt and not till this change is completed will the hydrated double

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[1] Vriens. Ibid. 7, 194 (1891).

salt begin to dissociate. If there is an excess of magnesium sulfate this will effloresce with formation of the hexahydrate and this salt will probably lose water before the double salt does.

The effect of diminished external pressure on the double iodid of lead and potassium deserves a moment's consideration. The new solid phase at the two quintuple points is not known but it must be anhydrous lead iodid[1] or another double salt containing less water than the first and possibly less lead iodid. If the solid phases at one of the quintuple points are lead potassium iodid, hydrated and anhydrous lead iodid and, at the other, lead potassium iodid, potassium iodid and anhydrous lead iodid a mixture of hydrated double salt and hydrated lead iodid will effloresce to hydrated double salt, hydrated and anhydrous lead iodid. When the hydrated lead iodid has entirely disappeared the hydrated double salt will begin to effloresce, forming anhydrous lead iodid and potassium iodid. The pure hydrated double salt or a mixture of this with potassium iodid will effloresce with the formation of the monovariant system, hydrated double salt anhydrous lead iodid and potassium iodid, the double salt finally disappearing entirely.

If the solid phases at one of the quintuple points are lead potassium iodid, a second double salt with or without water of crystallization and hydrated lead iodid and, at the other, the two double salts and potassium iodid, a mixture of lead potassium iodid and hydrated lead iodid will effloresce with formation of the second double salt at the expense of the first.[2] When lead potassium iodid has entirely disappeared the hydrated lead iodid will begin to effloresce. If the second double salt contain water of crystallization and anhydrous lead potassium iodid can not exist, the second double salt will begin to effloresce when all the hydrated lead iodid is gone, and there will be formed the divariant system, anhydrous lead iodid, potassium iodid and water vapor. A mixture of lead potassium iodid, PbI_2KI2H_2O, and potassium iodid will effloresce on the same assumption, with formation of the second double salt at the expense of the first, the

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[1] It has been shown, Jour. Phys. Chem. 1, 342 (1897), that anhydrous lead iodid can not be the phase but the assumption is tolerated because it might be correct if the temperatures of the quintuple points were reversed.

[2] If Pb = K in the second double salt.

second efflorescing in its turn and the final result being the divariant system, anhydrous lead iodid, potassium iodid and water vapor. The first double salt, if pure, will pass into the second double salt and then this will change into the two single iodids in case the ratio of lead to potassium is unity. If this is not the case, the first double salt will change into the second double salt and hydrated lead iodid. It is evident that an examination of the products of efflorescence will often give definite information as to the nature of phases existing at quintuple points which can not be easily investigated in the usual manner.

It must be remembered that all this reasoning is based on the assumption that the dissociation curves do not intersect. Since two adjacent dissociation curves always have two solid phases in common, an intersection would form a new quintuple point with four solid phases in equilibrium with vapor. If the four solid phases be denoted by the letters w, x, y and z respectively, the five curves meeting in the quintuple point will represent the simultaneous pressures and temperatures for the five monovariant systems: w, x, y and vapor; x, y, z and vapor; y, z, w and vapor; z, w, x and vapor; w, x, y and z. No instance of such a quintuple point has yet been observed. If such an one shall ever be found, there may then be a temperature below which a given binary or ternary compound can not exist. Such cases occur in one component systems, when one solid modification changes into another with evolution of heat and contraction of volume. In binary systems no such case has yet been found so that it is not surprising that none are known for ternary systems.

The results of this paper may be summed up:

1. A solid phase containing two components effloresces with formation of the solid phase which can coexist at the next higher quadruple point.

2. Two solid phases containing three components effloresce with formation of the solid phase which can coexist at the next higher quintuple point.

3. From a study of the effloresence products one can draw conclusions as to the phases existing at the quintuple points.

Cornell University, September 1896.

OSMOTIC PRESSURE AND VARIANCE

BY J. E. TREVOR

I. The Problem

Components. The starting point of Gibbs's thermodynamic theory of chemical equilibrium is the differential equation[1]

$$d\varepsilon = t d\eta - p dv + \mu_1 dm_1 + \mu_2 dm_2 + \ . \ . \ . + \mu_\nu dm_\nu$$

expressing the relation holding among the differentials of the energy, entropy, volume, and masses of the several components of a «phase» of its substances. The ν components can be chosen in any way compatible with the condition that the differentials of their masses shall be independent and shall express every possible variation in the composition of the phase.[2] Gibbs shows further[3] that when h relations subsist among the units of these components, the number of «independently variable components» of the phase is

$$n = \nu - h, \qquad (1)$$

and that the same is true of any system of phases taken as a whole,

This matter of the relation between the *components* and the *independently variable components* of a system has been put very clearly and completely by Gibbs,[3] but in so abstract a manner that its signification can be well comprehended only by readers gifted with imagination and trained into a thoroughgoing familiarity with the pertinent facts. Bancroft has accordingly done an important service[4] in lucidly stating the relation and in giving it illustration by all manner of application to material systems of various types. It has also been clearly and correctly employed in special cases in the thermodynamic studies of Duhem.[5]

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[1] Gibbs. Trans. Conn. Acad. 3, 116 (1875).

[2] l. c. 117.

[3] l. c. pages 120 and thereafter.

[4] Bancroft. The Phase Rule, 227 (1897).

[5] Duhem. Dissolutions et mélanges, Trav. et mém. des fac. de Lille.

Osmotic Systems. The gain in practical comprehension so made led Bancroft one step further[1] to the very interesting conclusion that since the introduction of osmotic walls into a material system may increase the number of pressures there, the $n + 2$ variables in Gibbs's formulation for the number of degrees of freedom or the *variance* of the system[2]

$$v = n + 2 - r$$

are thereby increased to $n + 2 + a$, when the addition of osmotic walls introduces a new pressures.[3] He thus recognized that the variance of a system containing osmotic pressures is changed in a perfectly definite manner by the appearance of these pressures.[4]

An advance in this direction is very important, for it lightens the difficulties hitherto attendant upon treating the osmotic phenomena in their proper connection with the simpler types of equilibrium with which they are allied—it is a step toward a more comprehensive classification by variance than has hitherto been possible. But upon closer examination of the matter in its present state one readily sees that the subject requires treatment in a more general way, for through the introduction of osmotic walls into a material system the $n + 2$ Gibbsian variables are, in the general case, increased by the

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[1] Bancroft. l. c. 235.

[2] Gibbs. l. c. 153 (1876).

[3] Gibbs. l. c. 138.

[4] The terminology of Variance used here has been employed by the writer for some years in all matters relating to a classification of material systems according to the number of their degrees of thermodynamic freedom (see this Journal, **1**, 167, and also Bancroft, Phase Rule, pp. 3 and 4). According to it all $(n + 2)$-phase systems of the ordinary phase rule are nonvariant systems, all $(n + 1)$-phase systems are monovariant ones, all n-phase systems are divariants, $(n - 1)$-phase systems are trivariants, and so on; one may also refer to systems of variance greater than unity as polyvariants, which is often convenient.

A pure liquid with its saturated vapor constitutes therefore a one-component monovariant system, an unsaturated solution with vapor is a two-component divariant, a mixture of two gases is a trivariant, and so on. It is shown in this paper that in osmotic systems the variance is not necessarily

$$v = n + 2 - r,$$

and it is readily seen also that the same is true of many voltaic combinations.

appearance of new potentials as well as by that of new pressures.[1] The manner in which this circumstance must be taken into account shall now be considered.

II. The Generalized Phase Rule

1. No Osmotic Walls. To find the number of degrees of freedom of the thermodynamic behavior of a system, from the number of its independently variable components and that of its phases, Gibbs considers the differential equation for the energy of any one phase

$$d\varepsilon = t d\eta - p dv + \sum_{1}^{\nu} \mu dm ; \qquad (2)$$

integrating this, over a change in the quantity of substance from zero to the given finite amount, at constant state (of temperature, pressure and composition),

$$\varepsilon = t\eta - pv + \sum_{1}^{\nu} \mu m, \qquad (3)$$

and then differentiating for the likewise perfectly general expression

$$\begin{aligned} d\varepsilon &= t d\eta - p dv + \sum_{1}^{\nu} \mu dm \\ &\quad + \eta dt - v dp + \sum_{1}^{\nu} m d\mu, \end{aligned} \qquad (4)$$

which in combination with (2) gives

$$0 = \eta dt - v dp + \sum_{1}^{\nu} m d\mu, \qquad (5)$$

indicating that there exists for each phase a relation

$$f(t, p, \mu_1, \mu_2, \ldots \mu_\nu) \qquad (6)$$

which is easily shown to be « fundamental » in Gibbs's sense. The variables appearing in (6) maintain uniform values throughout a system of r coexistent phases, and h relations obtain among the ν potentials, so [equation (1)]

$$(\nu - h) + 2 = n + 2$$

variables remain independent for each phase and they are subject to r conditions—to as many conditions as there are equations among

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[1] Gibbs, l. c. 138

them. The number of degrees of freedom or the variance of the system is therefore

$$v = n + 2 - r. \qquad (7)$$

2. *One Wall and No Separation.* In the cases thus treated by Gibbs there are however no osmotic pressures, the proof supposes the equilibrium pressures to have the same values at all coexistent phases. A simple case where this is no longer true is afforded by a two-component system of solvent and solute, separated into two portions by an osmotic wall permeable only for the solvent. These separated portions must now be regarded as individual phases, which involves a slight extension of Gibbs's definition. The attraction between the solute and the solvent will then establish an osmotic pressure upon one side of the wall, which will necessarily differ from the equilibrium pressure upon the other; the fundamental equations for the r phases of the system will then become—denoting by I the phases on the osmotic side of the wall, by II those on the other and by subscript l and s the solvent and solute respectively[1]—

$$\left.\begin{array}{l} f^{(1)}_{I}\ (t, p_{I}, \mu_{(s)}, \mu_{(l)}, \ . \ . \ . \ \mu_{n}) = o \\ f^{(2)}_{I}\ (t, p_{I}, \mu_{(s)}, \mu_{(l)}, \ . \ . \ . \ \mu_{n}) = o \\ . \ . \ . \\ f^{(r-1)}_{II}(t, p_{II}, \quad \mu_{(l)}, \ . \ . \ . \ \mu_{n}) = o \\ f^{(r)}_{II}\ (t, p_{II}, \quad \mu_{(l)}, \ . \ . \ . \ \mu_{n}) = o. \end{array}\right\}$$

It is here supposed, for the sake of simplicity, that the h extra components have already been eliminated. There are in these equations n potentials, one temperature and two pressures, $n + 3$ variables in all and r relations holding among them, so the variance of the system is

$$v = n + 3 - r. \qquad (7a)$$

This formulation is the phase rule for systems of the type considered.

The result may be illustrated by a system made up of a salt in water on one side of the osmotic wall and pure water with its vapor on the other, each component may be supposed kept at constant

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[1] The l and s might relate to 'liquid' and 'salt'.

volume by a closely fitting piston. The attraction between the salt and the water will draw water into the solution compartment until the osmotic pressure so produced there will have attained a value dependent upon the concentration. The concentration can be varied at constant temperature and the pressures will vary with varying temperature, so the equilibrium of the system is a divariant one although it has three, or $n + 1$, phases[1]. The addition of a new phase, as for example ice in the water compartment or solid salt in that of the solution[2], must diminish the variance by unity, and we readily see from the arrangement indicated by Fig. 1 that the concentration of the solution, and consequently the osmotic pressure, can not be varied at constant temperature,—such change can be due to the change of temperature only, the system is monovariant. This follows immediately from (7*a*), for $n = 2$ and $r = 4$ so that

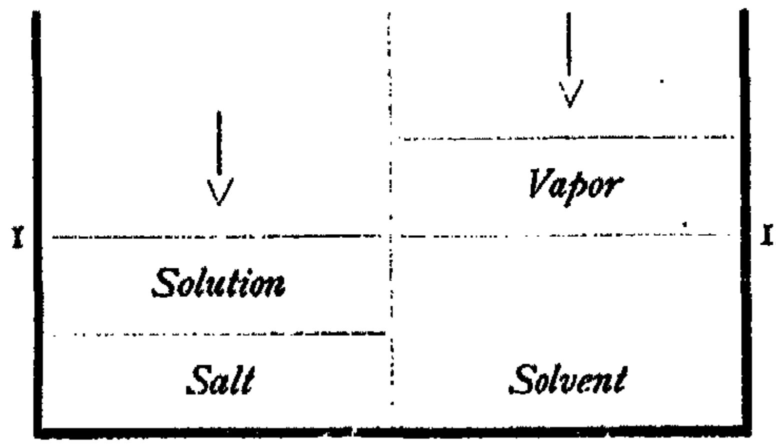

Fig. 1.

$$\begin{aligned} v &= n + 3 - r \\ &= 1. \end{aligned}$$

With the appearance of ice this system would become nonvariant; with solution on one side and solvent on the other it would be trivariant, and this appears also from the equation, which for $n = 2$ and $r = 2$ gives

$$\begin{aligned} v &= 2 + 3 - 2 \\ &= 3. \end{aligned}$$

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[1] Bancroft. Phase Rule, 235.

[2] The appearance, under ordinary circumstances, of a vapor phase on the side containing solution is excluded, because the pressure there is greater than the vapor pressure of the pure liquid.

3. One Wall and One Separation. The determination of variance in cases like those just cited is the matter elucidated by Bancroft, but we pass to the introduction of new potentials as well as of new pressures when we consider cases in which the substances for which the wall is impermeable are present in phases separated by the wall. Under such circumstances the fundamental equations of the phases are

$$\left.\begin{array}{l} f^{1}_{I}(t, p_{I}, \mu_{(1)I}, \mu_{(2)}, \ldots \mu_{n}) = 0 \\ f^{2}_{I}(t, p_{I}, \mu_{(1)I}, \mu_{(2)}, \ldots \mu_{n}) = 0 \\ \ldots \\ f^{r-1}_{II}(t, p_{II}, \mu_{(1)II}, \mu_{(2)}, \ldots \mu_{n}) = 0 \\ f^{r}_{II}(t, p_{II}, \mu_{(1)II}, \mu_{(2)}, \ldots \mu_{n}) = 0\,. \end{array}\right\}$$

There are here $n + 1$ potentials, one temperature and two pressures, $n + 4$ variables in all and consequently a variance of

$$v = n + 4 - r. \qquad (7b)$$

Suppose for example the four-phase system represented in Fig. 2

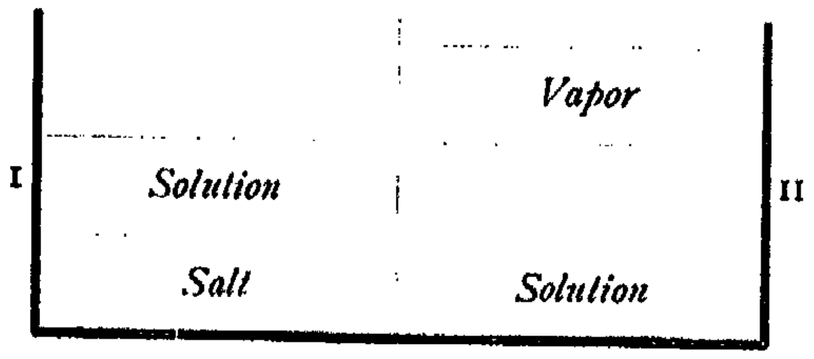

Fig. 2.

The two solutions will have in general different compositions and accordingly different potentials of their components, the concentration and pressure of the solution in II only can be varied at constant temperature, so the equilibrium is a divariant one ; this follows from (7b), which for $n = 2$ and $r = 4$ becomes

$$\begin{aligned} v &= 2 + 4 - 4 \\ &= 2 \end{aligned}$$

as stated. The transfer to a monovariant system may be made through the appearance of ice in the unsaturated solution, the system then assuming the monovariant equilibrium of a fusion curve. With the freezing of ice from the compartment I the two sides of the system would become identical and the influence of the osmotic wall upon the equilibrium phenomena would disappear. This circumstance is illustrated more simply by the appearance of salt in II, above, with increasing concentration there. We should then have, as in Fig. 3, the phases of solid salt identical and also those of solution, so that the two masses of salt for example form one phase as truly as do individual crystals of the salt and the situation is in no wise altered if the volume be increased so as to permit the appearance of a second mass of the vapor phase. The solutions must eventually come to the same level through the influence of gravity ; the pressures and potentials are the same on each side of the membrane and the variance is simply $n + 2 - r$ or $2 + 2 - 3$, a monovariance, just as if the membrane were not present. Such identity of phases and consequent disappearance of osmotic pressures must not be overlooked in variance problems where osmotic walls are concerned. A similar state of affairs appears when a solution with other possible phases is separated by like osmotic walls from two different compartments containing pure solvent, with or without vapor,—the outside compartments contain but a single set of phases and so but one osmotic wall comes really into the consideration. This may also be shown, if it be so desired, by writing out the fundamental equations for all the phases.

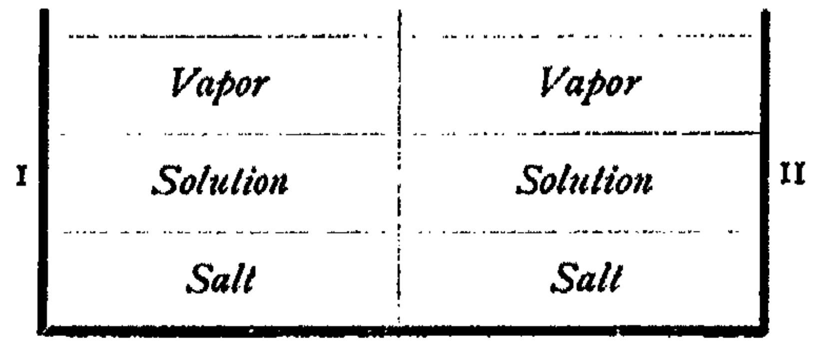

Fig. 3.

4. Two Like Walls and One Separation. An increased complexity is reached by the introduction of two osmotic walls into a system, we will first consider these walls to be impermeable for the same components. The set of fundamental equations for the phases of such a system, when it is supposed that the outside compartment III contains no solute, are

$$\left.\begin{array}{l}
f^{1}_{I}(t, p_{I}, \mu_{(1)I}, \mu_{(2)}, \ldots \mu_{n}) = 0 \\
f^{2}_{I}(t, p_{I}, \mu_{(1)I}, \mu_{(2)}, \ldots \mu_{n}) = 0 \\
\ldots \\
f^{r-1}_{II}(t, p_{II}, \mu_{(1)II}, \mu_{(2)}, \ldots \mu_{n}) = 0 \\
f^{1}_{II}(t, p_{II}, \mu_{(1)II}, \mu_{(2)}, \ldots \mu_{n}) = 0 \\
\ldots \\
f^{r-1}_{III}(t, p_{III}, \quad \mu_{(2)}, \ldots \mu_{n}) = 0 \\
f^{r}_{III}(t, p_{III}, \quad \mu_{(2)}, \ldots \mu_{n}) = 0\, .
\end{array}\right\}$$

There appear here $n - 1 + 2$ potentials, one temperature and three pressures, or $n + 5$ variables in all with the consequent variance of

$$v = n + 5 - r. \qquad (7c)$$

The simple arrangement, under this head, which is represented in Fig 4, has one possibility of a variation of an equilibrium pressure at constant temperature, namely by changing, directly or by additional pressure, the composition of the solution in I. The system is therefore divariant,—and this result follows from equation (7c), for with $n = 2$ and $r = 5$

$$\begin{aligned} v &= 2 + 5 - 5 \\ &= 2 \end{aligned}$$

a divariance. Changes of variance through the introduction or disappearance of phases, and simplification of the system by the appearance of identical phases upon both sides of a wall, are readily

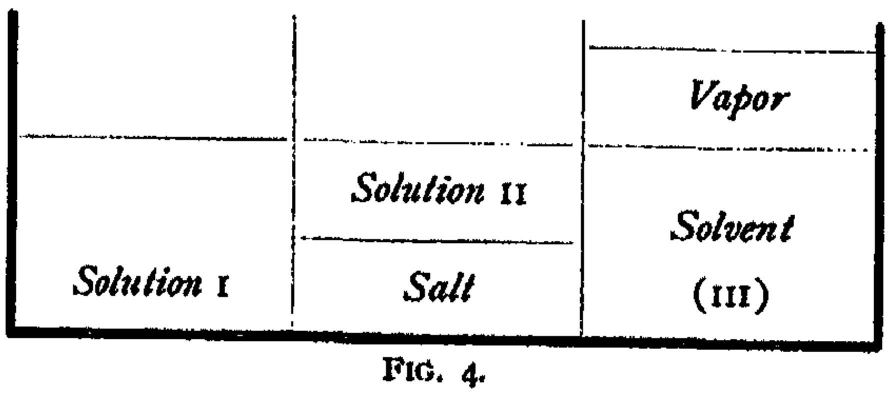

FIG. 4.

foreseen. Further, addition of solute to the compartment III is seen at once to introduce a new potential into the system and therefore to raise its variance by unity for any same number of phases.

5. Two Unlike Walls and No Separation. It should not be omitted to indicate at this point that the considerations employed in the foregoing hold in unchanged wise when the osmotic walls which appear in a given system are permeable not for the same but for different components.

Raoult has shown[1] that walls of vulcanized rubber are permeable for ethyl ether but not for methyl alcohol, while such of swine's bladder are permeable for the alcohol but not for the ether. It is therefore possible, with the aid of these membranes, to construct osmotic systems in which a mixture of the two substances named shall be in equilibrium with each of the pure components,—as is indicated in Fig. 5. We have here to do with two potentials, one temperature and three different equilibrium pressures, six variables in all with five phases, *i. e.* five relations holding among these variables; the variance is therefore $6 - 5 = 1$, a monovariance. The equilibrium pressures of the system can obviously not be varied isothermally, so changes with changing temperature alone arise for consideration, the equilibrium is actually a monovariant one.

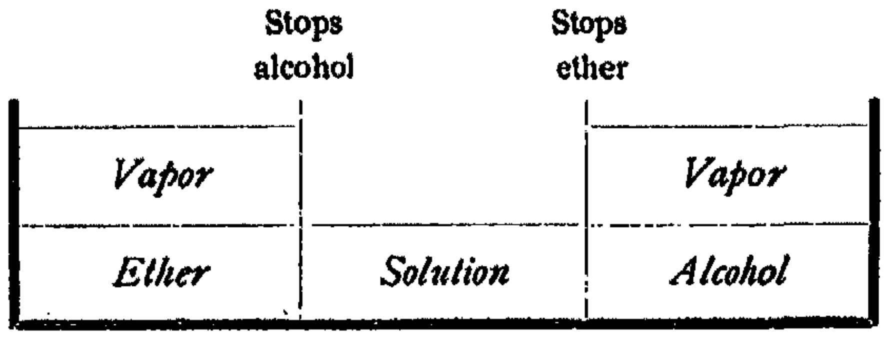

Fig. 5.

6. Two Unlike Walls and One Separation. The formation of a solution in one of the outer compartments of the above system must increase the variance by unity, of course; the process would produce for example the arrangement of Fig. 6. Here are two alcohol potentials, one for ether, one temperature and three pressures to be considered, seven variables with five relations among them—a

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[1] Raoult, Zeit. phys Chem. 17, 737 (1895).

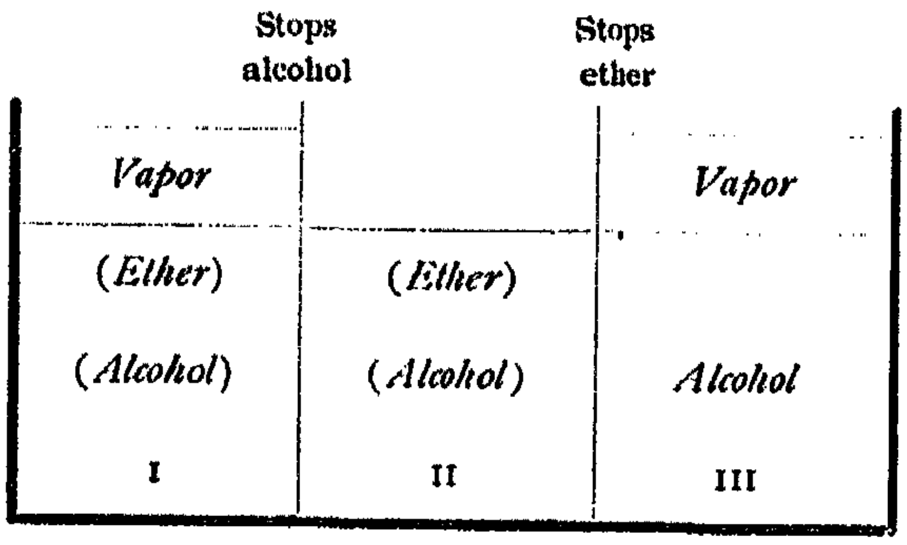

FIG. 6.

variance of two as was foretold. One observes readily that the state of the system can be varied in one way isothermally—by changing the concentration of the dissolved alcohol in I—and the temperature can be changed as well, the system is actually in a divariant state. Other variations, with the addition, abstraction or replacement of phases are readily imaginable.

7. *Complex Cases.* If, instead of adding a new phase of solid solvent or the like, one should carry out the allied process of adding yet another osmotic wall, impermeable for alcohol let us say, the very interesting case of Fig. 7 would arise. Here the state of affairs

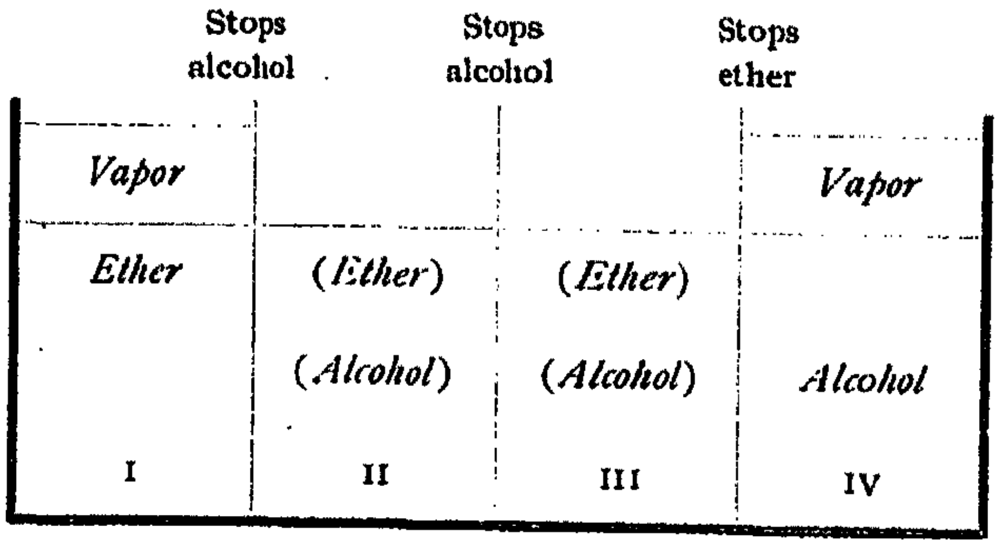

FIG. 7.

is governed primarily by the fact that the mass of alcohol in II is kept constant there by the walls of the cell. This circumstance causes the establishment of a definite equilibrium with the pure solvent in I, for any given volume of II. The solution of ether in alcohol in III, on the other hand, will come to equilibrium with the alcohol of IV, the resulting pressure in III depending upon the volume and the amount of ether there. When II and III are, finally, set in communication they must come to an equilibrium between themselves which can only be when the composition of the latter becomes equal to that of the former—for ether can pass from I to III (or the reverse) and the displaced alcohol in III can flow out into IV. The two solutions will yet stand under different pressures, because, although they seem to have the same composition, one of them is in equilibrium with ether and the other is so with alcohol. The resulting equilibrium of the entire system is governed by the relative mass of the alcohol in II, which can be varied at constant temperature, the entire system of pressures will vary of course also with the temperature so the system is a divariant one. That such is the result of the theory is shown by counting the variables,—one potential for ether, two for alcohol, one temperature and four different pressures,—eight variables and six phases, with a resulting variance of two as shown by the experimental examination.

In connection with such cases it is instructive to consider the similar arrangement in which the separating osmotic walls are all of the same kind and impermeable for one component, say the solute. Such a system is presented in Fig. 8. Here the concentrations in II and in III are in general different, so these two compartments must stand under different pressures to be each in equilibrium with the solvent and the vapor. This too is compatible with equilibrium between II and III. For suppose $p_{\prime\prime\prime} > p_{\prime\prime}$; then, for given volumes of each of these two phases, the attraction of the solute in II, $S_{\prime\prime}$, for the pure solvent, plus the difference of the attractions

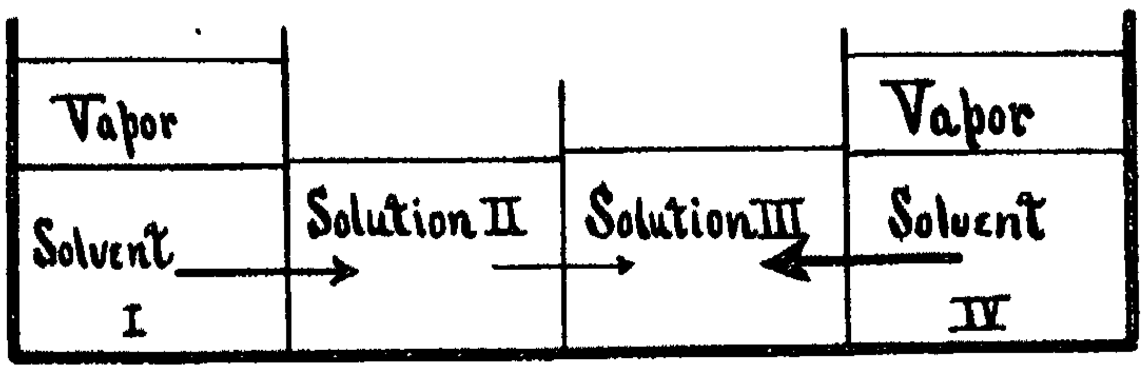

FIG. 8.

which the solute in III, $S_{'''}$, has for the solvent in II and $S_{''}$ has for that in III, are exactly counterbalanced by the attraction which $S_{''}$ has for the solvent in IV. This is indicated by the medium, light and heavy arrows in the figure. The compartment II with its two membranes may in fact be regarded as constituting a single membrane impermeable for the solute, the attraction of this latter for the pure solvent is then the same—from III—in either direction and it is immaterial how the pressure changes in the interior of the membrane. In such treatment the volume and mass of solute in II need not be supposed constant, that is to say the osmotic pressure is independent of the nature of the membrane.[1] The total result would be altered in no wise if the two end compartments should be connected directly, thus forming in appearance as they do in fact but one phase each of pure liquid and of vapor.

It will be remarked that only combinations of two components have been discussed in the above illustrations, the application of theory to systems of more than two components would seem to offer no especial difficulty.

8. The Generalized Phase Rule. It is now desirable, after the general canvass which has been made of the field, to condense the above considerations into a rule for determining the variance of any given osmotic system from its osmotic peculiarities and the number of its components—into a logical extension of the phase rule. To do so we have merely to note that the variance is always the total number of variables which a system exhibits, diminished by the number, r, of its phases. The variables are n potentials, being at least one for each independently variable component, one for the temperature and one for at least one pressure, with x for the added pressures introduced by the appearance of x osmotic walls[2] and y for each of the y *separations* of a component by such a wall.

The total number of variables is therefore

$$n + 2 + x + y$$

and the variance is

---

[1] Compare, in connection with this, van 't Hoff, Zeit. phys. Chem. 9, 477 (1892).

[2] Save when a set of phases is simply reproduced and two pressures become equal.

$$v = n + 2 + x + y - r.$$

This is the generalized phase rule, as applicable to systems containing osmotic pressures. For the limiting case in which all osmotic walls are absent we have both $x = 0$ and $y = 0$ and consequently the Gibbsian variance of

$$v = n + 2 - r.$$

III. *Test of the Rule*

To test the correctness of this formulation and at the same time illustrate the convenience, the readiness, of its application let us apply it successively to the cases adduced in the foregoing section. Following the previous order and numbering we have, first, for single walls and no separations,

Solution	*Vapor*	(1)
Salt	*Solvent*	

one extra pressure and no separations, $n = 2$, $x = 1$, $y = 0$,

$$\begin{aligned} v &= 2 + 2 + 1 + 0 - 4 \\ &= 1, \end{aligned}$$

a monovariant; then, when the solution is unsaturated,

	Vapor	(1*a*)
Solution	*Solvent*	

$$\begin{aligned} v &= 2 + 2 + 1 + 0 - 3 \\ &= 2, \end{aligned}$$

a divariant; next, when the solvent freezes,

	Vapor	
Solution	*Ice*	(1*b*)
Salt	*Solvent*	

$$\begin{aligned} v &= 2 + 2 + 1 + 0 - 5 \\ &= 0, \end{aligned}$$

a nonvariant; and finally when the solution and solvent are present alone,

Solution	*Solvent*	(1*c*)

$$v = 2 + 2 + 1 + 0 - 2$$
$$= 3,$$

the system is a trivariant. For single walls with one separation there were considered

Solution	*Vapor*	(2)
Salt	*Solution*	

$$n = 2 \qquad x = 1 \qquad y = 1$$
$$v = 2 + 2 + 1 + 1 - 4$$
$$= 2,$$

the system is divariant; but in

	Vapor	
Solution	*Ice*	(2*a*)
Salt	*Solution*	

$$n = 2 \qquad x = 1 \qquad y = 1$$
$$v = 2 + 2 + 1 + 1 - 5$$
$$= 1,$$

it is monovariant. The system (3) introduced no new pressures and no separations, so we pass to (4) with two walls and one separation,

	Solution II	*Vapor*	
Solution I	*Salt*	*Solvent*	(4)

$$n = 2 \qquad x = 2 \qquad y = 1$$
$$v = 2 + 2 + 2 + 1 - 5$$
$$= 2,$$

a divariant; then the same with two separations,

	Solution II	*Vapor*	
Solution I	*Salt*	*Solution III*	(4*a*)

$$n = 2 \qquad x = 2 \qquad y = 2$$
$$v = 2 + 2 + 2 + 2 - 5$$
$$= 3,$$

a trivariant. With two unlike walls and no separation we considered

Vapor		*Vapor*	
Ether	*Solution*	*Alcohol*	(5)

$$n = 2 \qquad x = 2 \qquad y = 0$$

$$\begin{aligned} v &= 2 + 2 + 2 + 0 - 5 \\ &= 1, \end{aligned}$$

a monovariant; and with one separation,

Vapor		*Vapor*	
Solution I	*Solution II*	*Alcohol*	(6)

$$n = 2 \qquad x = 2 \qquad y = 1$$

$$\begin{aligned} v &= 2 + 2 + 2 + 1 - 5 \\ &= 2, \end{aligned}$$

a divariant. For the «complex cases» we have

Vapor			*Vapor*	
Ether	*Solution II*	*Solution III*	*Alcohol*	(7)

$$n = 2 \qquad x = 3 \qquad y = 1$$

$$\begin{aligned} v &= 2 + 2 + 3 + 1 - 6 \\ &= 2, \end{aligned}$$

the system is a divariant; and, finally, with like membranes we have the case

Vapor			*Vapor*	
Solvent	*Solution II*	*Solution III*	*Solvent*	. (8)

The two end compartments here have been shown (as is indeed now apparent from inspection) to constitute but a single pair of phases, so that they might in fact be connected by a canal without disturbing the equilibrium; accordingly

$$n = 2 \qquad x = 2 \qquad y = 1$$

$$\begin{aligned} v &= 2 + 2 + 2 + 1 - 4 \\ &= 3, \end{aligned}$$

the system is trivariant. This is obviously true, for the equilibrium pressures can be varied in two ways isothermally, by changing the concentrations of either of the inside compartments.

The variance as thus determined accords in every case with that worked out in the preceding section. Any number of further combinations might be added, but it is believed that those given are sufficient for the present purpose. It may be well nevertheless to add, in closing, that two-component systems can be arranged with vapor alone or with vapor and ice in one of their compartments: Imagine for example the system depicted in Fig. 9; the solution, supposed sufficiently concentrated, may be allowed to expand until it shall have absorbed entirely the relatively small amount of solvent in II, and it may then be brought into equilibrium with the unsaturated vapor of II by suitably altering the pressure. The consequent variance will be that conditioned by one extra pressure and no separation, namely

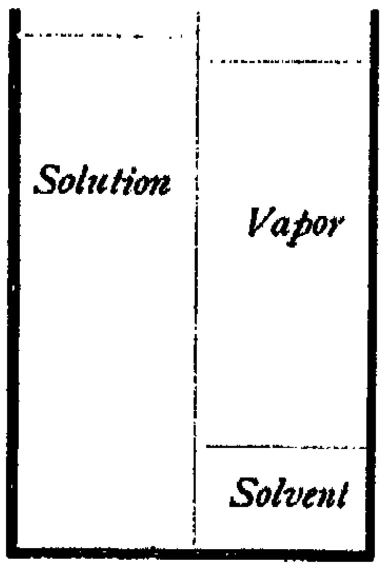

Fig. 9.

$$v = 2 + 2 + 1 + 0 - 2$$
$$= 3,$$

a trivariance[1],—and it would be reduced to a divariance by cooling the system to the temperature at which ice appears in the vapor compartment. It is well worth while to reflect upon such cases when studying osmotic phenomena.

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[1] It will be noted that the pressure of the vapor will not in general be that of the saturated vapor of the solution as it stands.

IV. Close

The peculiar advantage accruing from definite determination of the variance of sytems containing osmotic pressures is that the relations of the equilibria of such systems to those of the simpler types of thermodynamic equilibrium where osmotic pressures do not appear become thereby apparent. One may classify the equilibria with which physical chemistry is concerned in two ways, which offer, each of them, decided advantages; one can classify either primarily according to the variance and secondarily according to the number of independently variable components—thus treating all monovariant systems together, then all divariants and so on—or classify primarily according to the number of independently variable components and secondarily according to the variance. When following the latter plan one completes the discussion of one-component systems before attacking that of two-component systems; and under the head of two-component systems one can begin the treatment of osmotic phenomena, and discuss them in the order of the variance of the equilibria in hand. The whole scheme of presentation becomes thereby very orderly and coherent, and it has for these reasons much to recommend it for lucidity and consequence. But without due attention to the variance of osmotic systems it is a difficult and an arbitrary matter to introduce the important phenomena, which they present, into a satisfactory treatment of thermodynamic equilibria in particular or of physical chemistry in general.

Cornell University, December 1896.

NEW BOOKS

Lehrbuch der allgemeinen Chemie. *W. Ostwald. Second edition. Vol. II, 2; part 1. Large octavo, 208 pages. W. Engelmann; Leipzig, 1896. 5 marks.* The first part of the long expected volume on chemical affinity has appeared at last and the rest of the book is promised us before the end of this year in three or four instalments. Most people will rejoice at the decision to issue the volume in parts instead of as a whole. To read one thousand pages at one time is a task that few of us undertake and very few accomplish.

In this number the sketch of the historical development of the doctrine of chemical affinity covers two hundred pages and is divided into two equal parts, the early and the modern development. In the first we find a review of the work of Berthollet, 1799, Deville and Debray, 1857, Berthelot and Péan de St. Gilles, 1862, Williamson, 1851, Clausius, 1857 and Pfaundler, 1867, on chemical equilibrium; of Biot, 1835, and Gladstone, 1855, on optical relations; of Thomsen, 1857, and Berthelot, 1867, on thermochemistry and of Wilhelmy, 1850, on reaction velocity. Modern history begins with the deduction of the mass law by Guldberg and Waage, 1867, and the application of thermodynamics to chemical processes by Horstmann, 1869. Thirty-five pages are devoted to a review of Gibbs's thermodynamical studies, 1876, and then we have the work of van 't Hoff, 1884, on the change of the equilibrium with the temperature; the determination of affinity constants by Thomsen, 1869, and by Ostwald, 1877; van 't Hoff's application of the gas laws to solutions, 1885, and the dissociation theory of Arrhenius, 1887.

The least familiar and, therefore, the most interesting portion of the number is the part devoted to Willard Gibbs. Ostwald is one of the very few people who have read Gibb's paper without skipping a single word, and it was to be hoped that he would give us a clear and accurate account of what Gibbs found and how he found it.

This hope has not been realized. There is nothing to show that the italicized passage on page 115 is right and yet the proposition is not self-evident. Gibbs's proof, page 116, that the chemical potential for each component must be constant throughout the system when each component occurs in every phase and no chemical reaction takes place, is copied omitting the cases, elaborately discussed by Gibbs, in which these limitations are done away with. The «fundamental» equations of Gibbs are all integral equations and not differential equations as is implied on page 121. The deduction of the Phase Rule from the heat, volume and chemical energies, page 126, is not correct unless the relations among the p's, t's and μ's have been established and then it is superfluous. There is a tacit assumption of the conclusion which it is required to prove. It is rather surprising to find here and on page 142 references to the ease with which an already discovered relation can be deduced from the principles of energetics, when one remembers the recent paper by Boltzmann on this very subject. It should also be kept in mind that Ostwald, and not Gibbs, is responsible for the statement that the capacity factor for chemical energy is the combining weight—an assumption in support of which no evidence has yet been advanced.

The last dozen pages of this instalment form the first part of the chapter on reaction velocities and contain data for the inversion of cane sugar (Wilhelmy); for the action of potassium permanganate on oxalic acid and of hydrogen peroxid on hydriodic acid (Harcourt and Esson); for the catalysis of methylacetate (Ostwald) and for the action of water on dibromsuccinic acid and monochloracetic acid (van 't Hoff). At first sight it seems natural to begin with the approaches to equilibrium and then to study the phenomena of equilibrium. Guldberg and Waage started from the kinetic theory of gases and deduced an expression for the velocity of reaction. According to this view there could be equilibrium only when the rate of formation of one system was equal to the rate of decomposition of the same system, and it was therefore natural to broach the subject of chemical affinity by a discussion of velocities. On the other hand we do begin our studies of chemistry, either as individuals or as a race, by examining cases of equilibrium. Most chemists never get beyond a study of qualitative equilibrium and the physical chemist passes, in the laboratory, from qualitative to quantitative equilibrium and then to a study of the laws describing the phenomena of change. There seems to be no good reason why the teaching of the text-book should reverse the teaching of the laboratory. It is urged by some that we must consider equilibrium as a dynamic phenomenon, involving the balancing of two velocities; but this is not true. There is no balancing of velocities when a voltaic cell is opposed by an electromotive force equal to its own and yet there is equilibrium. This conception is a relic of the kinetic theory of gases and it is surprising to find Ostwald, of all people, adopting it. For our purposes, it is better to start from the theorem of Wenzel, 1777, quoted by Ostwald, page 40, that «the strength of the chemical action is proportional to the concentration of the reacting substances». That is the most general and the most accurate statement of the mass law which can be made to-day.

Wilder D. Bancroft.

Vorlesungen über Bildung und Spaltung von Doppelsalzen. *J. H. van 't Hoff and T. Paul. Octavo, 95 pages. W. Engelmann; Leipzig, 1897. Price, 3 marks; bound, 3.50 marks.* The first part of this book is devoted to general theory, the second to a description of methods and the third to an account of some of the systems which have been studied experimentally. Under general theory we have the behavior of a system made up of two salts and water at constant temperature and at changing temperature; the pressure and the electrical phenomena for the same system. In the second part we have the five chief methods of determining the inversion temperature: with the diatometer, the tensimeter, the galvanometer, the thermometer and by a study of the solubility curves. The systems referred to in the third section are those in which the two salts are sodium and magnesium sulfates, potassium and magnesium sulfates, copper and potassium chlorids and the various tartrates and racemates.

This is a very interesting program but there one must stop. The proper way to treat the subject is to give the exact theory first and then to help oneself out by assumptions. The Phase Rule gives an absolute classification, though a purely qualitative one. It would next be in order to show that under certain circumstances it was possible to make approximate quantitative predictions. Instead of this, the author has based his treatment upon the theory of dilute solutions and the Nernst solubility theory without even mentioning the Phase Rule. Since none of the solutions considered are dilute solutions and since the general relations hold, whether the addition of the second salt increases or decreases the solubility of the first, it is clear that the entire deduction is misleading and inaccurate.

The book does not give a complete statement of our knowledge in regard to the formation and decomposition of double salts. Roozeboom's work on ferric chlorid and hydrochloric acid is ignored; there is no reference to the theorem of van Rijn van Alkemade in regard to temperature changes along boundary curves nor to Schreinemakers's rule for cryohydric points, while the discussion of evaporation at constant temperatures is limited to the very uninteresting case where the crystals are not removed from the solution. These omissions are intentional for it is stated in the preface that the lectures on which the book is based were intended to give an account of the work in the Amsterdam laboratory. One may be a firm believer in the advantages of the historical method and yet not endorse this position. Whatever one may do in a book, lectures should be based on scientific and not on geographical divisions of the subject. The reviewer is a great admirer of van 't Hoff; but he cannot blind himself to the fact that, in the book in question, the subject is presented in an incomplete way from a point of view which is out of date. *Wilder D. Bancroft*

Théorie thermodynamique de la Viscosité, du Frottement et des faux Équilibres chimiques. *P. Duhem. 8 vo, 210 pages. A. Hermann; Paris, 1896.* The present volume is a reprint from the *Mémoires de la Société des Sciences physiques et naturelles de Bordeaux* (5) **2** (1896), and as such, especially also because of its size and of the fully rounded treatment of its subject, it may well be regarded as a book instead of a journal article. In connection with it one should note a recent paper by L. Natanson, on irreversible processes, reviewed in the present number of this Journal, page 374.

In the introduction of the paper (pp. 1–16) it is shown that although equilibrium always subsists when according to the principles of ordinary thermodynamics it should subsist, yet the converse statement is not true—equilibria may obtain when change is to be expected, the so-called «false equilibria». Analogous phenomena appear in mechanics, where change may be hindered by friction, and it is shown that, analytically considered, both types of rest fall into the same category. It is the object of the present paper to enlarge thermodynamic theory in such wise as to make it account for both the ‹true› and the ‹false› equilibria. To do so the author is led, by logical reasoning, to reject the «fundamental assumption of thermodynamics», that the outer actions which can maintain a state of equilibrium are completely determined by the equations known as the ‹conditions of equilibrium› of the system. He maintains, however, that certain supersaturation and retardation phenomena, being certainly due to capillary action, are not false equilibria in his sense at all.

Part I of the book treats Viscosity. After an historical sketch (pp. 17–19), closed systems at constant temperature T are taken up (pp. 20–23), which T together with the ‹normal variables› $\alpha, \beta, \ldots, \lambda$ define the state. $\mathfrak{F}$ is the free energy, $\mathfrak{T}$ the kinetic energy, and $A, B, \ldots L$ are the outer actions; then

$$A + \frac{\partial(\mathfrak{T} - \mathfrak{F})}{\partial\alpha} - \frac{d}{dt}\frac{\partial\mathfrak{T}}{\partial\dot{\alpha}} + f_\alpha = 0$$

and similarly for β, *etc.* The f_α, f_β, *etc.*, are the «resistances of viscosity»; their work must be zero or negative, from which follows $\int dQ/T > 0$ for closed cycles in the latter case. Q is heat evolved. The same result is carefully established for systems whose parts have different temperatures and bilateral interrelations (pp. 24–41), and it is followed by discussion of the more general case where relations with exterior bodies appear (pp. 41–48). The remainder of Part I treats the movement of a continuous viscous medium (pp. 49–56), and the influence of viscosity on diffusion—a general expression, equations (71), being reached, which reduces to Fick's equation on assuming slow diffusion, a nearly homogeneous system and a medium sufficiently viscous to admit of neglecting the quantities $\partial^2\rho/\partial t^2$; ρ = partial density (pp. 57–66).

Part II is ostensibly devoted to friction. New variables $a, b, \ldots l$, are defined by putting their variations and fluxes

$$\delta a = \mu_{11}\delta\alpha + \mu_{12}\delta\beta + \ldots + \mu_{1n}\delta\lambda$$
$$\dot{a} = \mu_{11}\dot{\alpha} + \mu_{12}\dot{\beta} + \ldots + \mu_{1n}\dot{\lambda}$$

and similarly for $b, \ldots l$; the coefficients are n^2 functions of $\alpha, \beta \ldots \lambda$, whose determinant

$$\begin{vmatrix} \mu_{11} & \mu_{12} & \ldots & \mu_{1n} \\ \ldots & & & \\ \mu_{n1} & \mu_{n2} & \ldots & \mu_{nn} \end{vmatrix}$$

is not zero. As consequences of the «fundamental assumption» (see above) of thermodynamics the author derives

$$\mathfrak{A}\delta a + \mathfrak{B}\delta b + \ldots + \mathfrak{L}\delta l,$$
$$J_a\delta a + J_b\delta b + \ldots + J_l\delta l,$$
$$\varphi_a\delta a + \varphi_b\delta b + \ldots + \varphi_l\delta l,$$

as the work of outer actions, of inertia and of viscosity respectively, and consequently as the equations of motion of the system

$$\begin{cases} \mathfrak{A} - \Phi_a + J_a + \varphi_a = o \\ \ldots \\ \mathfrak{L} - \Phi_l + J_l + \varphi_l = o. \end{cases}$$

Dropping the «fundamental assumption» these equations each obtain a term of the form $g_a \dfrac{\dot{a}}{|\dot{a}|}$ — where $|\dot{a}|$ denotes the absolute value of $\dot{a}$ — such that the sum of these new terms, times dt, is the work done by friction during dt. The theory then indicates for closed systems a series of states not foretold by ordinary thermodynamics, and that in closed cycles with friction, be the temperature uniform or not, $\int dQ/T > o$ (pp. 67–88), and it is then made to supply general equilibrium equations for systems with neglected viscosity (pp. 89–98).

To further discuss false equilibria the variables fixing the state are reduced to α, together with the temperature T and constant pressure P. With no friction relative to α,

$$\frac{\partial}{\partial\alpha} H(P, \alpha, T) = o$$

where H is the thermodynamic potential, the equation represents the «curve of true equilibria» at the pressure P. *With* friction it is shown that

$$\Phi - \mathfrak{A} = \partial H/\partial\alpha,$$

which reduces the above general equations to

$$\frac{\partial H}{\partial\alpha} - \varphi - g\frac{\dot{\alpha}}{|\dot{\alpha}|} = 0 \quad .$$

With γ the (negative) limit which $g(P,\alpha,T,\dot{\alpha})$ approaches as α approaches zero, the condition of equilibrium is

$$\gamma \leqq -\partial H/\partial\alpha \leqq -\gamma,$$

and we get two curves

$$\partial H/\partial\alpha + \gamma = 0 \quad (1) \qquad \partial H/\partial\alpha - \gamma = 0 \quad (2)$$

and as condition of stability of the false equilibria

$$\partial^2 H/\partial\alpha^2 > 0.$$

It therefore follows :—1. The curve (1) lies wholly above, and (2) wholly below, that of the true equilibria, γ being essentially negative ; 2, The strip between (1) and (2) is the region of false equilibria, and the curve of the true ones is traced entirely within the region of the false ones ; 3, The system is not in equilibrium in the regions below (2) and above (1),—in the former α increases during spontaneous change, and it decreases in the latter. The theory is then recast for the condition of constant volume instead of that of constant pressure ; (pp. 99–104).

For detailed examination and application of these results it is supposed that the two positive functions

$$-\gamma(P,\alpha,T) \qquad\qquad -\Gamma(V,\alpha,T)$$

decrease continuously with rising temperature, *i. e.*, that the two curves limiting the region of false equilibria are far from the curve of true ones at low temperatures, but approach the letter asymptotically as the temperature rises. The «point of reaction» is the point of transition out of the region of false equilibria as the temperature rises. The consequences of the theory are then elaborately worked out, applied to experimental cases and illustrated graphically by curves, the treatment being concluded by a study of equilibria in unequally heated spaces, (pp. 104–126).

The next chapter is, naturally, on the velocities of reactions. The theory is shown to require $d\alpha/dt$ to be positive, negative or zero in the regions of combination, of dissociation and of equilibrium respectively, and formulations for these velocities are found; the phenomena of abrupt coolings and heatings close the chapter (pp. 127–138). These matters are continued in a chapter on explosions, where the question of stability in all cases of adiabatic disturbance of state is treated analytically, graphically, and with reference to experiment. Extended examination is then given to acceleration of reactions and to explosion waves (pp. 139–182).

In the concluding chapter, on Friction, the author drops a previous restriction, that the system studied shall be continuous or their parts bound together, reaching thereby results of the same general character as before. The treatment throughout the volume is clear and exact and the subject is a very interesting one which has hitherto received but little attention, the paper certainly marks an important advance. *J. E. Trevor*

Theorie der Luftschwingungen in Röhren mit offenen Enden. *H. Helmholtz (1859). No.* 80, *131 pp., 2 marks.* **Experimental-unter-suchungen über Elektricität.** *Michael Faraday. I. and II. Reihe (1832). No.* 81, *96 pp., 1.50 marks.* **Systematische Entwicklung der Abhängigkeit geometrischer Gestalten von einander.** *Jacob Steiner. 1 Theil. No.* 82, *126 pp., 2 marks; 2 Theil. No. 83, 162 pp., 2.40 marks. Ostwald's Klassiker der exakten Wissenschaften; W. Engelmann. Leipzig, 1896.* We take pleasure in announcing the appearance of four new volumes of Ostwald's now well known *Klassiker* series. A. Wangerin edits the Helmholtz paper, and A. J. v. Oettingen the others. All are carefully annotated. The little volume of Faraday will be especially welcomed in these days of electrochemical investigation. *J. E. T.*

REVIEWS

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

General

On the Laws of Irreversible Phenomena. *L. Natanson. Bull. Acad. Cracovie* **1896**, *117*; *Phil. Mag.* [*5*] **41**, *385* (*1896*); *Zeit. phys. Chem.* **21**, 193 (*1896*). The author treats the quantitative laws of irreversible phenomena, as an extension of Hamilton's Principle. The treatise is divided into two parts; in the first a statement of the principle is made and a number of particular cases are discussed. The second brings an affirmative answer to the question: Does a general law exist concerning the infinitesimal expressions ($d'Q$ and $\delta'Q$) which characterize the dissipation of energy in the particular cases taken up?

The state of a system at the time t being determined by the variables q_i, the work done by external forces in any variation is $\Sigma P_i \delta q_i$, and the heat absorbed is $\Sigma R_i \delta q_i$; the corresponding differential expressions are $\Sigma P_i dq_i$ and $\Sigma R_i dq_i = dQ$. This dQ is the sum of reversible and irreversible parts, $d^\circ Q + d'Q = dQ$, which on considering the δq_i become the variations $\delta^\circ Q + \delta' Q = \delta Q$.

Now Hamilton's Principle of Varying Action, as stated by the author, is

$$\int_{t_0}^{t_1} dt(\delta T - \delta U + \Sigma P_i \delta Q_i + \delta' Q) = o, \qquad (I)$$

it is commonly written in the form

$$\delta \int_{t_0}^{t_1} (T - V) dt = \left\{ \sum \frac{\partial T}{\partial \dot{q}} \partial q \right\}_{t_0}^{t_1},$$

where the term $\sum \frac{\partial T}{\partial q} \delta q$ is considered as pushed to the limits. The author speaks of it as the «thermokinetic principle». The Lagrangian equations become

$$\frac{d}{dt}\frac{\partial T}{\partial s_i} - \frac{\partial T}{\partial q_i} + \frac{\partial Q}{\partial q_i} - P_i - R_i = o \qquad \text{(II)}$$

where T and U are the two parts of the energy and the s_i are the velocities $\partial q_i / \partial t$; these equations have been given implicitly by Helmholtz, explicitly by Duhem, and for a particular case by Rayleigh. From the equations (I) and (II) the expression for the conservation of energy is obtained

$$dT + dU - \Sigma P_i dq_i - dQ = o,$$

the reverse deduction is of course not possible. Through a generalization of the idea of free energy, and with the aid of certain auxiliary assumptions, the author arrives at another expression for the principle, namely

$$\int_{t_0}^{t_1} dt \left[\delta T - \sum \frac{\partial V}{\partial q_i} \delta q_i + \Sigma P_i \delta q_i + \delta' Q \right] = o \qquad \text{(III)}$$

where V is the potential energy. From these three equations the author derives the particular forms which they take in reversible thermodynamics, irreversible dynamics, irreversible hydrodynamics, diffusion, heat-conduction and electromagnetic dissipation.

In the second part of the paper the differential coefficient $d'Q/dt$ is tentatively put equal to $-2F$, whose quantity F in irreversible dynamics is Rayleigh's «dissipation function». It is then stated that of dF/dt the portion DF/Dt, which is the rate of «coercion» or of the action tending to efface disturbances, appears as proportional to F and we have $DF/Dt = -2F/\tau$, where the period of time τ is the generalized «time of relaxation» of Maxwell. The author verifies this relation in the cases of irreversible hydrodynamics, diffusion, electromagnetic dissipation, irreversible dynamics and heat-conduction. He finally shows simple relations to hold among the periods τ and concludes: «In a similar manner may all the periods of relaxation, corresponding to the various powers of coercion of a given body, be mutually connected; and every such simple equation, if it holds, is equivalent to a definite law.» *J. M. Talmadge.*

A New Form of Pyknometer. *J. C. Boot. Jour. Am. Chem. Soc.* **19**, *61* (*1897*). A glass pyknometer with double walls, the space between them being exhausted. The instrument described contains 25 c. c. and weighs about 30 grams. *J. E. T.*

Determination of the Atomic Masses of Silver, Mercury and Cadmium by the Electrolytic Method. *W. L. Hardin. Jour. Am. Chem. Soc.* **18**, *990* (*1896*). Carefully purified and well crystallized salts of the several metals were dissolved in water (usually with addition of potasssium cyanid) and the metal was precipitated upon a platinum dish by a carefully regulated electric current. All weighing were reduced to vacuum. The following values were assumed in the calculations of atomic mass: H = 1.008, C = 12.01, N = 14.04, O = 16, Cl = 35.45, Br. = 79.95. Results obtained from silver oxid, silver succinate and mercuric oxid were unsatisfactory. With silver nitrate, acetate and benzoate was found as final mean Ag = 107.925. For mercury and cadmium, beside the method described above, an attempt was made to utilize Faraday's law, that equivalent weights of different metals are precipitated by the same current. Each of these metals was precipitated from double cyanid solution at the same time with silver, whose atomic mass was assumed to be 107.92. The final means were: Hg = 199.985 ; Cd = 112.0465 by the former method, or 111.952 by the latter. *R. B. W.*

The Cooling of the World as First Cause of Evolution. *R. Quinton. Comptes rendus,* **123**, *1094* (*1896*). In a previous note the author showed that the appearance of warm-blooded animals was a necessary consequence of falling temperature. In the present note he shows the relation between temperature and the methods of reproduction. He believes that if the world had kept the temperature which it had when the fishes and reptiles alone existed, neither birds nor mammals would ever have appeared. *W. D. B.*

On the Development of Fungus in a Moving Liquid. *J. Ray. Comptes rendus,* **123**, *907* (*1896*). In a vessel half full of liquid and subjected to a continual oscillation, a spore of *Sterigrmatocystis* developed a spherical form with a tendency to a cell structure, instead of growing in the normal manner. *W. D. B.*

On a Simple Automatic Sprengel Pump. *B. B. Boltwood. Am. Chem. Jour.* **19**, *76* (*1897*). A portable automatic mercury pump which can be set up wherever there is a good water pump. It is made by Goetze in Leipzig and seems to be a most admirable piece of apparatus. *W. D. B.*

Monovariant Systems

On the Potential Energy and the Virial of the Molecular Forces, etc. *G. Bakker. Zeit. phys. Chem.* **21**, *497* (*1896*). Extended molecular-theoretical calculations to find the «potential energy» of a liquid and the «virial of the molecular forces». It is concluded that the ratio of the heat of vaporization to the difference between the densities of liquid and of vapor is proportional to the «square of the molecular diameter»,—whatever that may mean. Tables are adduced to show that this ratio is actually independent of the temperature, for water, ether, chloroform, nitrous oxid, carbon dioxid and sulphur dioxid, over ranges of from fifty-five to one hundred fifty degrees. *J. E. T.*

On Corresponding Temperatures (under Equal Vapor Presures). *J. A. Groshans. Wied. Ann.* **60**, *169* (*1897*). An article supporting the author's law of corresponding temperatures. The analytical expression of the law is

$$\frac{T}{T_o} = \frac{T'}{T'_o} = constant,$$

where T, T' are the boiling temperatures, on the absolute scale, of any liquid at any two pressures, and T_o, and T'_o are the boiling temperatures, on the absolute scale, of water at pressures corresponding to T and T'.

In the twenty-four examples given the agreement is fair, the maximum difference between calculation and observation being four percent. *C. L. S.*

Supplementary Remarks upon the Paper on Freezing-points of Binary Mixtures. *A. Dahms. Wied. Ann.* **60**, *119* (*1897*). A heavily italicized reply to Roloff, based upon new measurements with carefully purified benzene and acetic acid. Science would have been a gainer if the author had been less interested in his polemic and had studied the rise of freezing point which occurs when water is added to a solution of acetic acid in benzene in insufficient quantities to form a second liquid phase. As it is, his previous results are confirmed and nothing more. *W. D. B.*

Action of Hydrochloric Acid Gas on the Alkali Sulfates. *A. Colson. Comptes rendus*, **122**, *1285* (*1896*). When hydrochloric acid gas acts upon sodium sulfate there is formed the monovariant system, Na_2SO_4, $NaHSO_4$, NaCl and vapor; then the divariant system $NaHSO_4$, NaCl and vapor and, with increasing concentration of hydrochloric acid, the monovariant system, $NaHSO_4$, NaCl, solution and vapor. The author has determined the vapor pressures of the two sets of monovariant systems at different temperatures. *W. D. B*

Solubility Determinations for Salts of Capronic and Oenanthylic Acids. *E. Altschul. Monatsheft Wien* **17**, *567* (*1896*). The solubility curve for the calcium salt of oenanthylic acid passes through a minimum at about 47°. According to the author there is a sudden change in the direction of the curve at this point and yet he offers no suggestions as to the nature of the solid phases. It is a clear case of a man trying to do work for which he was not fitted.

W. D. B.

Divariant Systems

The Specific Gravities of Water Solutions of Formic Acid. *G. M. Richardson and Pierre Allaire. Am. Chem. Jour.* **19**, *149* (*1897*). A table giving the specific gravities, together with the percentage composition by weight and by volume, of one hundred solutions at 20°C. The volume contractions for a series of ten solutions appear in an appended table. *J. E. T.*

An Attempt to Determine the Adiabatic Relations of Ethyl Oxide. *E. P. Perman, W. Ramsay and J. Rose-Innes. Roy. Soc. Proc.* **60**, *336* (*1896*). (*Abstract*). Determinations of the wave length of sound in gaseous and liquid ether at temperatures between 100° and 200°C, pressures between 4000 mm and 31000 mm mercury, and volumes between 2.6 c.c. and 71 c.c. per gram. It is found that

$$E = gT - h,$$

where E is the adiabatic elasticity and g and h are functions of the volume only. It had been found earlier, in conjunction with Young, that for ether and other substances a similar linear relation holds between pressure and temperature at constant volume,

$$p = bT - a,$$

so now by elimination of T one can express E as a linear function of p for constant volume. The coefficient, g/b, of p is found from the experimental data to be practically constant. The resulting differential equation is integrated and a set of adiabatic curves is drawn—the first adibatics obtained for any substance not an ideal gas. The mathematical work is due to Rose-Innes. *J. E. T.*

A New Method for Determining Slight Differences in Vapour Tension. *M. Reinganum. Wied. Ann.* **59**, *764* (*1896*). With a view to throwing light on the problem of the rise of sap in trees, Professor Askenasy, Verh. naturhist. med. Vereins zu Heidelberg, N. F. **5**, has devised the following striking experiment. With a layer of plaster of Paris he closed the mouth of a funnel whose tube was about one meter long, filled the tube and funnel completely with a saturated solution of plaster of Paris, and stood the apparatus upright, with the lower end of the tube dipping into a trough of mercury. As the water gradually evaporated at the surface of the plaster cup the mercury rose in the tube, in one case attaining a height of 893 mm (in fifteen hours) while the barometer stood at 753 mm. The experiment generally came to an end by the formation of an air bubble, gradually drying up of the plaster, and sinking of the mercury.

M. Reinganum shows that by the aid of a construction analogous to that employed by Arrhenius for deducing the relation between osmotic pressure and vapor pressure, an expression may be obtained connecting the height of the mercury column with the vapor pressure of the aqueous vapor in the air surrounding the plaster cap. The same relation may be obtained directly, as Nernst suggests, by equating the quantity of work (A), gained during the isothermal distillation of one gram molecule (18 g) of water from p, the vapor pressure of the solution in the tube, to p', the pressure of the aqueous vapor in the air surrounding the cap, to the quantity of work (B) necessary to raise an equal volume (viz. 18 c.c.) of mercury (sp.gr. 15.96) to the height h of the mercury column in the apparatus at equilibrium,

$$RT \log nat\, p/p' = h \times 18 \times 15.96 \times g.$$

Reinganum suggests the employment of the apparatus as a means of measuring extremely small differences in the vapor pressure of solutions. An idea of the delicacy of the method may be gained from the calculation, that a difference of 0.001 mm between the tension of the solution in the tube and the tension of aqueous vapor in the atmosphere surrounding the cap, would cause the mercury to rise almost four centimeters (at 17°C). *W. L. M.*

Solution and Diffusion of Certain Metals and Alloys in Mercury. Second Paper. *W. J. Humphreys, Jour. Chem. Soc.* **69**, *1679* (*1896*). Cadmium and thallium diffuse into mercury very readily, antimony and aluminum practically not at all. An alloy containing ninety per cent copper and ten per cent tin behaved like a block of pure copper, while brass scarcely diffused at all. This gives us another method for distinguishing between pairs of metals which do not form solid solutions and those which do. It would be very interesting to dissolve brass in mercury and then let it diffuse into pure mercury. *W. D. B.*

The Alloys of Copper and Zinc. *G. Charpy. Nature* **55**, *130* (*1896*). When copper or brass has been hardened by rolling and then annealed, the mechanical properties depend upon the maximum temperature of annealing. The curve representing the change of the tensile strength with the temperature of annealing is made up of three parts. In the two end ones the tensile strength varies very little with the temperature of annealing; in the middle one very much. The temperature at which the effect of annealing becomes noticeable is lower the more thoroughly the sample is hardened.

Alloys of copper and zinc form a continuous series of solid solutions up to thirty-five per cent of zinc. Since the compound Cu_2Zn contains about thirty-four per cent of zinc the author draws the unwarrantable conclusion that the alloys containing less than this amount of zinc are mixtures of copper and Cu_4Zn. The alloy corresponding to the formula $CuZn_4$ solidifies as a homogeneous mass; but it is impossible from this paper to decide whether there is really such a compound. The presumption is against it, the author's views to the contrary notwithstanding. *W. D. B.*

On the Rôle of Boric Acid in Glasses and Enamels. *L. Grenet. Comptes rendus,* **123**, *891* (*1896*). The opposite effects upon the coefficient of expansion caused by the presence of boric acid are due to the fact that with continued addition of boric acid the coefficient decreases, passes through a minimum and increases. If an excess of boric acid be added to melted glass, two liquid layers are formed. *W. D. B.*

On the Absorption of Hydrogen Sulfid by Liquid Sulfur. *H. Pélabon. Comptes rendus,* **124**, *35* (*1897*). Hydrogen is not absorbed to a perceptible amount by liquid sulfur; the two react with formation of hydrogen sulfid, the solubility of which increases with rising temperature. The author makes the very improbable statement that with falling temperature none of the gas is given off until the sulfur solidifies. This is interesting but confusing. *W. D. B.*

On the Freezing-point of Milk. *J. Winter. Comptes rendus,* **123**, *1298* (*1896*). The theory of the author that cow's milk freezes at − 0.55° has been disputed by Bordas and Génin. In reply the author publishes freezing-point determinations for some fifty samples of milk taken from nearly as many cows. In only two cases was there a variation of as much as 0.02° from the mean depression of 0.55°. *W. D. B.*

Polyvariant Systems

An Attempt to Separate the two Components of Clèveite Gas by Diffusion. *A Hagenbach. Wied. Ann. 60, 124* (*1897*). Independently of Ramsay and Collie, Comptes rendus, **123**, 214, 542 (1896), the author succeeded in obtaining from helium two gases having the same spectrum but different densities. *W. D. B.*

Researches on the Sulfids of Cobalt and Nickel. *G. Chesneau. Comptes rendus,* **123**, *1068* (*1896*). When a cobaltous salt is acted upon by a solution of an alkaline polysulfid saturated with sulfur there is formed Co_4S_7. *W. D. B.*

On the Absorption of Nitric Oxid by Ferrous Bromid. *V. Thomas. Comptes rendus*, **123**, *943* (*1896*). Below 10° aqueous ferrous bromid absorbs nitric oxid with formation of $3FeBr_2,2NO$; at 15° with formation of $2FeBr_2.NO$. *W. D. B.*

Action of Ammonia on the Bichlorid of Tellurium. *R. Metzner. Comptes rendus*, **124**, *32* (*1897*). At 200° ammonia gas reduces the bichlorid of tellurium with formation of ammonium chlorid, nitrogen and metallic tellurium. At 0° there is formed the addition product, $TeCl_4 3NH_3$ while at $-15°$ it is possible to get the compound TeN. The author's work is purely qualitative; but a careful quantitative study of this system would seem well worth while.

W. D. B.

Synthesis of Hawksite. *A. de Schulten. Comptes rendus*, **123**, *1325* (*1896*). From a hot solution of the sulfate and carbonate of sodium there crystallizes the salt $Na_2CO_3 4Na_2SO_4$. The author has isolated this by precipitating with sodium hydroxid and washing with alcohol. *W. D. B.*

Solubility of Alkali Haloids in Presence of the Free Acid. *A. Ditte. Comptes rendus*, **123**, *1281* (*1896*). Data for the precipitation of potassium and sodium fluorids by hydrofluoric acid. With each salt the solubility passes through a minimum. *W. D. B.*

Solubility of Alkali Haloids in Presence of the Free Base. *A Ditte. Comptes rendus*, **124**, *29* (*1897*). Data for the precipitation of potassium bromid by potassium hydroxid and of sodium bromid by sodium hydroxid. The values given are grams of the two solids in one thousand grams of water. With sodium bromid there is a break at the point where the anhydrous salt appears. The author does not state how he made his analyses. *W. D. B.*

Velocities

An Analytical Investigation of the Hydrolysis of Starch by Acids. *G. W. Rolfe* and *G. Defren. Jour. Am. Chem. Soc.* **18**, 869–

900. (Oct., 1896). In numerous and varied experiments, 100 grams of good commercial starch were mixed with a liter of water containing the hydrolyzing acid, and heated under a pressure of two to four atmospheres. Samples were withdrawn from time to time, neutralized, filtered, and tested for specific rotatory power and cupric reducing power. The estimate of total solids in the polarized solution was based upon specific gravity, assuming an increase of 0.00386 for each gram in 100 c.c. of solution; but since the increase is 0.00390 for maltose and 0.00381 for dextrose, the corrections are made in estimating the specific rotatory power for these bodies; $[a]_{D386}$ being 195° for dextrin, 135.2° for maltose[1] and 53.5° for dextrose. The authors have plotted corresponding values of specific rotatory power as abscissas, and cupric reducing power as ordinates; and they conclude that from 195° to 90°, the results outline an arc of a circle, (see Note A). The latter part of the curve is not so well defined; perhaps from the formation of «reversion products».

Very pretty curves are drawn to show the relative quantities of dextrin, maltose and dextrose at each stage of the conversion, as based upon the curve described; the maltose rising to a maximum at about 129°, while dextrin and dextrose are equal at nearly the same stage.

A few commercial analyses are reported; and where the usual relation between rotatory and reducing power is observed, normal hydrolysis is inferred; otherwise, the sample is supposed to represent a mixture of two separately converted products.

For the rapid determination of the conversion of commercial glucose, permanent standards are suggested, in imitation of the usual iodin tint as observed by the workmen; and a convenient logarithmic table is printed, to calculate rotatory power.

Samples were withdrawn from the autoclave after certain intervals of time, in order to calculate the speed of the reactions. It is assumed that the starch is first dissolved as amylodextrin; and that this is then changed to maltose, and (at the same time) maltose converted to dextrose. Each of these two changes seems to the authors to follow Wilhelmy's inversion formula; some rather wide variations

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[1] Ost gives the specific rotatory power of maltose as $[a]_D^{20°} = 137.04 \pm 0.19°$; see Wiley's "Agricultural Analysis," **3**, 206.

in «constants» being attributed to variations in temperature. (See Note B.) The subject of «reversion» at higher stages is still open. The hydrolyzing values of several acids are compared with Ostwald's velocity constants; and the influence of time, of temperature, of concentration, and of the several acids, is shown by diagrams.

While recognizing the excellent work represented in this paper, and the difficulties successfully encountered, the reviewer would add a few comments. The misprints or other numerical errors are very perplexing; but the authors are correcting these for the *Technology Quarterly*, and few of them need claim our attention here. I take this opportunity to thank Mr. Rolfe for friendly correspondence and explanations on several points.

Note A. The authors do not explain how they compute their equation for the circle from experimental data. They appear to have counted abscissas from the initial rotation, making $x = 195° - [a]$, and $y = K$. The circle

$$x^2 + y^2 - 747x + 757y = 0$$

would then pass very nearly through the extreme and middle points of the curve indicated by Table C. Wiley gives linear formulas for the same relation (for denser solution) in Proc. Am. Ass. 1880, page 309; a slight curvature is clearly indicated in these later experiments, as plotted; but the more usual interpolation formula may be more convenient and equally trustworthy, either

$$x = Ay + By^2, \quad \text{or} \quad y = Ax + Bx^2.$$

Note B. In seven series out of the twelve, the values computed for c_1 show an increase as the reaction proceeds, varying from 10% to 34% of the mean value, the increase for all the series being (on the average) nearly 14% of the several means. This seems to imply that the fundamental equation must be modified or differently applied. The values of c_2 usually pass a minimum, and then show a marked increase.

It seems improbable that the conversion and solution of starch ceases before the dextrin begins to change to maltose. Had the authors published the specific gravity of each solution, as taken from the autoclave, it would be interesting to trace any change in the quantity of total soluble ingredients. The whole theory might embrace at least four simultaneous changes, namely,

1. Starch to dextrin, etc.
2. Dextrin to maltose.
3. Maltose to dextrose.
4. The formation of those «reversion products,» which are not very clearly indicated unless in the higher stages.

As regards the first of these changes, if starch is continuously converted into dextrin, the result would be to increase the relative amount of dextrin in the later stages, or to diminish the calculated values of the coefficient of speed for its conversion into maltose, contrary to the observations. If, however, the starch is partly hydrolyzed in advance of solution, so that undissolved matter is directly converted into maltose, *etc.*, at the later stages, this might account for the apparent increase in the coefficient of speed, as noted. Special experiments in this direction are still wanting.

If the equations

$$\frac{dm}{dt} = c_1 d \quad \text{and} \quad \frac{dg}{dt} = c_2 m$$

express the assumptions that dextrin changes into maltose at a rate proportional to the quantity of dextrin present, and maltose into dextrose at a rate proportional to the quantity of maltose present, it is clear that when maltose reaches a maximum,

$$\frac{dm}{dt} = \frac{dg}{dt},$$

therefore, $c_1 d = c_2 m$, that is, the coefficients of speed are inversely proportional to the quantities of active substance present, when the intermediate product reaches a maximum. But, at this point, we find by Table C (corrected) that d is about 27.4% and m about 46.2% ; hence we should expect to find c_2 equal to about $0.6 c_1$; but c_2, as computed proves to be 1.6 to 1.9 times c_1. In fact, the authors have used common logarithms instead of natural logarithms, and all their values for c_1 should be multiplied by 2.3026, in order to make them comparable with corresponding values of c_2. *R. B. W.*

Note on the Review «On the Esterification of Aromatic Acids» by Bredig. *R. Wegschneider. Zeit. phys. Chem.* **21**, *302*

(*1896*). Upon the assertion of Bredig that Wegschneider, from the same mechanistic premises concerning esterification as those of V. Meyer, had arrived at an opposed conclusion, the author remarks that he utilized this fact to declare the insufficiency of the method employed by Meyer, his idea agreeing therefore essentially with that of his reviewer. *J. E. T.*

The Catalytic Action of Metals on the Inversion of Cane Sugar. *B. Rayman and O. Sulc. Zeit. phys. Chem.* **21**, *481* (*1896*). When sugar is warmed with pure water in platinum vessels, at 60° to 100C°, the inversion is at first very slow, but afterwards becomes more rapid, possibly owing to the formation of an intermediate optically inactive sugar. In glass vessels the inversion takes place much more slowly than in those of platinum, copper or silver. Addition of small quantities of finely divided palladium, rhodium, osmium or platinum increases the rate (palladium has the most effect, the others in the order given) while iridium diminishes it.

On long boiling in the presence of palladium part of the sugar is oxidized with formation of formic acid and of a non-volatile acid, possibly lactic. The paper closes with an account of the decomposition of fructose and glucose by water at high temperatures.

W. L. M.

Electromotive Forces

Hall Effect in Liquids. *F. Florio. Nuovo Cimento*, 4, *106* (*1896*). The Hall effect is not to be detected in a solution of zinc sulfate; Roiti has maintained the same, Bagard the contrary. *J. E. T.*

Potential Differences between Metals and Electrolytes. *O. Wiedeburg. Wied. Ann.* **59**, *742* (*1896*) Let T be the surface tension of a mercury electrode, φ the potential difference between it and the electrolyte, then,

$$\frac{dT}{d\varphi} = -e$$

In this equation, e has the dimensions of a quantity of electricity divided by a surface. According to the Lippman and Helmholtz theories, e is the surface density of electricity on the ions of the electrolyte fronting the surface of the mercury. Helmholtz merely remarks that φ and e vanish simultaneously. Lippman, however, goes further in the development of this relation so that we may put

$$e = 2k\varphi \; .$$

Let T be any surface tension, T_m the maximum surface tension, then

$$T = T_m - k\varphi^2 \; .$$

But if A is the polarizing potential difference, φ_n the natural potential difference (the potential difference when the mecury electrode is very large and is reckoned mercury minus electrolyte), J a possible current through the whole circuit whose resistance is W, then, reckoning φ in a direction opposite to that in which φ_n is reckoned, we have

$$\varphi = A - \varphi_n - JW$$

whence

$$T = T_m - k(A - \varphi_n - JW)^2 \; .$$

Accordingly, the surface tension of a mercury electrode at equilibrium will only be a maximum when there is no current at the time that the polarizing potential difference equals the natural potential difference. That is, only when

$$JW = o \quad \text{and} \quad A_m = \varphi_n$$

is T a maximum. In general

$$A_m = \varphi_n + JW$$

where A_m is the maximum value of A.

The maximum polarizing potential difference does not in general equal the natural potential difference between the mercury and electrolyte; to get the latter, the former is to be diminished by a quantity derived from a current through the circuit. This current may be produced by occluded matter, convection, and so on.

According to the writer, this current is not considered in the applications of the mercury electrode and to this oversight, is due the quite considerable divergence in the results obtained with the mercury electrode. Were this correction properly applied, the theory of Lippmann and Helmholtz would not be subject to such hostile criticism. *C. L. S.*

On Measurements of the Resistance of Electrolytes with Alternating Currents. *F. Kohlrausch. Wied. Ann.* **58**, *514 (1896); and M. Wien. Wied. Ann.* **59**, *267 (1896).* In a paper on «polarization by alternating currents», Wied. Ann. **58**, 37 (1896), M. Wien has calculated the error which may arise from this source in determining the electrical resistance of solutions; and, by way of illustrating his theory by an exteme case, has worked out an example in which an electrolytic resistance of ten ohms is supposed to be measured between unplatinized electrodes of ten square centimeters area—the error from polarization amounts to thirty per cent. of the value obtained.

While recognizing the importance of M. Wien's paper, Kohlrausch objects most strenuously to having the experiment in question labeled «Kohlrausch's Method»; and points out, with some emphasis, that no one who has ever read his (Kohlrausch's) papers on conductivity measurements could ever have conceived the ‹wonderful idea› of determining a resistance under the conditions of this experiment.

In reply M. Wien disclaims any intention of discrediting Kohlrausch's method; but, having been challenged, points out individual cases in Kohlrausch's work in which there is an error, due to polarization, of as much as 0.6 percent. As however the errors in question occur only among the earlier measurements, carried out with help of the dynamometer instead of the telephone; and as even there they can be detected only in a very few out of several hundred cases, the interest attaching to them is mainly owing to the illustration they afford of the new (Wien's) theory of the method.

W. L. M.

On the Passage of Carbon from the Non-conducting to the Conducting State. *G. Brion. Wied. Ann.* **59**, *715 (1896).* The electrical conductivity of carbon filaments, such as are employed in incandescent lamps, is much greater after they have been heated for some time to a high temperature (600°–1000°C); on standing in the cold their resistance increases again. The conductivity appears to depend only on the highest temperature to which they have been exposed, subsequent repeated heating to a lower temperature has little or no effect.

Of general applicability is the author's method of measuring the resistance of the filaments, which eliminates the variable resistances at the contacts between metal and carbon. *W. L. M.*

Theory of the Residual Current with Polarized Electrodes. *E. Salomon. Zeit. Elektrochemie*, **3**, *264*, (*1896*). Helmholtz showed that a small current always passes when acidulated water is electrolyzed between platinum electrodes with low electromotive forces. This case is not suited to quantitative treatment owing to the occlusion of hydrogen and oxygen by the electrodes. At the suggestion of Nernst the author deduces a set of formulas for silver electrodes in potassium nitrate solutions when different but known amounts of silver nitrate are added at the electrodes. The most serious objection to be made to the author's calculations is that he sets the electromotive force of polarization equal to the external electromotive force and yet if this were the case there could be no current. *W. D. B.*

Electrolysis and Electrolytic Dissociation

Electrical Conductivity of Heated Gases. *P. Pettinelli and G. B. Marolli. Rend. Acc. Lincei*, **5**, *136* (*1896*). Resistance measurements of gases in a porcelain tube at about 1200°C. The resistances do not follow Ohm's law, and they fall with rising porosity of the negative electrode. The observed peculiarities resemble those observed with the flame of a Bunsen burner. *J. E. T.*

On the Behavior of Bacteria with Chemical Reagents. *Th. Paul and B. Krönig. Zeit. phys. Chem.* **21**, *414* (*1896*). It has long been known that the salts of certain metals, *e.g.* silver, mercury, *etc.*, exert a specifically poisonous action on plant and animal cells, but although an enormous number of observations on the subject have been published, the individual experiments have been carried out under such very differing conditions that for the purposes of this paper the authors found it necessary to undertake a complete new series of measurements. In order that fairly concentrated solutions ($v = 16\,l$ or more) might be employed, the spores of *Bacillus Anthracis* were chosen as principal test object, this form being one of the most able to resist the poisonous action of the various salts.

The spores were distributed as equally as possible on small garnets; for each experiment thirty of these were placed for a measured time in the solution to be tested, then removed, washed, and the spores planted in gelatine. By counting the colonies of bacteria that appeared three days later, the relative poisonous effects of the various solutions employed were ascertained. All precautions were taken to keep the temperature and other circumstances the same throughout the whole research. A series of measurements with mercuric chlorid, in which the time of immersion varied from two minutes to two hours, and the concentration from $HgCl_2$ in 16 *l.* to $HgCl_2$ in 512 *l.* furnish the best evidence of the reliability of the results obtained by this method.

Among the most interesting results of the enquiry are the following:—

1. The bases, and in dilute solutions the acids, seem to act according to their electrolytic dissociation.
2. Nitric, chromic, chloric and permanganic acids act according to their position in the series of oxidizing agents as determined by electrochemical measurements. Chlorin has a marked individual action.
3. The halogen compounds of mercury, the cyanid and the sulpho-cyanate, stand in the order of their electrolytic dissociation.
4. Addition of other soluble chlorids, which reduces the dissociation of mercuric chlorid, also reduces its poisonous action; the slightly dissociated cadmium chlorid has the least effect in this direction.
5. Substances such as mercuric cyanid, the ammonia-silver, compounds, the soluble double cyanid of gold and of silver, *etc.*, whose solutions contain very few of the ions of the metals named, are almost non-poisonous.

In all, solutions of sixty-eight substances were experimented with; and although, as might be expected from the unavoidably variable nature of the bacteria employed as test objects, quantitative experiments in this department are attended with unusual experimental difficulties, and many questions raised by the research must be left for the present unanswered, yet the paper must be regarded as a most interesting and successful attempt to apply the modern theories of solutions to a biological problem, and the results obtained are a great step in advance of the view recently expressed by a bacteriologist of repute, that «the disinfecting value of the mercury compounds, call them by what name you will, depends on nothing but the quantity of soluble mercury they contain». *W. L. M.*

The Significance of the Arrhenius Dissociation Theory for Analytical Chemistry. *F. W. Küster. Zeit. Elektrochemie,* 3, *233, 257* (*1896*). After a general statement of the dissociation theory and the reasons for it, the author explains that the solvent action of acetic acid upon zinc, iron and lead sulfids is diminished by addition of sodium acetate because of the changes in the dissociation of the acetic acid and the consequent decrease of the concentration of hydrogen as ion. Attention is then called to the reasons for the fact that an excess of a precipitating agent decreases the solubility of the precipitate. The evolution of hydrochloric acid gas when sulfuric acid is added to a concentrated solution of hydrochloric acid is attributed to the change of the dissociation of the latter. (The question of the mutual solubilities of the two acids is entirely overlooked). The most interesting point in the paper is the effect of neutral salts upon solutions of hydrochloric and acetic acids with methylorange as indicator. Addition of sodium acetate to the acetic acid solution destroys the color while sodium chlorid has no perceptible effect upon the hydrochloric acid solution. *W. D. B.*

Electrical Furnaces for the Preparation and Purification of Metals. *W. Borchers. Zeit. Elektrochemie,* 3, *188, 213, 239, 260* (*1896*). We may classify all heating by electricity under two heads, when there is no arc formed and when there is one. In the first case one works with low voltage and heavy current; in the second with high voltage and a light current. The author puts in two subheads under each of these heads dividing the subject up as follows:

I. Heating due to resistance.

a. The substance to be heated is a part of the circuit.

b. The substance to be heated is in contact with a heated conductor.

II. Heating due to arc.

a. The substance to be heated forms one or both of the poles.

b. The substance in question is heated by the arc.

Ia. Although Pepys had converted iron wire into steel by heating it with a heavy current in presence of carbon as far back as 1815, the first practical furnace of this type is the Cowles furnace dating from 1884. Coke mixed with aluminum oxid and copper formed the resistance between two carbon electrodes. It was found that the same amount of aluminum was reduced whether the furnace was run by a direct or an alternating current. (To the reviewer this seems a reason for classifying the Cowles furnace under Ib since it seems only natural to take aluminum oxid as the substance to be heated. While it is true that «Cowles reduces aluminum oxid with electrically heated carbon» it is quite as necessary to heat the aluminum oxid as the carbon). Héroult electrolyzes melted aluminum oxid with a current heavy enough to keep the electrolyte fused. At first it was necessary to add copper to keep the aluminum formed from taking up carbon and the product was therefore aluminum bronze; but by a modification of the process, the details of which are not made public, it is now possible to obtain pure aluminum. Borchers has altered the Héroult furnace by changing the electrolyte, cooling the walls of the furnace and using, as cathode, a steel plate which is also cooled artificially. The Taussig furnace is entirely closed so that substances can be melted under any pressure or in any atmosphere.

Ib. Borchers constructed in 1891 a furnace in which the heavy carbon electrodes were connected by a small carbon rod round which was packed the substance to be heated. With this apparatus he was able to reduce all the oxids and to show that in many cases the reduction products reacted with the carbon. In the de Laval furnace the resistance is an electrolyte while the furnace of Crompton and Dowsing differs from the other two in that the substance to be heated is not in direct contact with the electrically heated resistance. Borchers calls attention to the fact that in furnaces of the types Ia and Ib it is important, from a commercial point of view, to know the «current density referred to the unit of weight of the conducting material in the unit of length of the resistance».

One of the greatest advantages of electrical heating is that the walls of the furnace do not need to be at the same temperature as the inside. When a furnace is heated from the outside the walls must be less fusible than the substance to be melted—a condition which it is not always easy to fulfil. With the electrical furnace there may easily be a difference of a couple of thousand degrees between different parts of the furnace.

IIa. The first practical furnace is due to C. W. Siemens, 1878. As at first made, the pole which was not intended to melt was placed above the crucible and was cooled artificially ; but it soon proved more practical to cool the lower electrode. The use of a solenoid to keep the arc in place is also due to Siemens and all the later furnaces of this type are merely variations upon his original idea. The only form which calls for mention is that of Slavianow in which both poles are fused.

IIb. The first patent for a furnace in which the substance to be heated is in a space heated by the arc was applied for in 1853 ; but the first practical furnace was made by Siemens in 1879. In this case as in the furnaces coming under the head IIa, the more recent inventions are adaptations of the principles formulated by Siemens. In the furnace of Lejeune and Ducretet the electrodes are inserted at an angle, there is a large space above the crucible into which gases can be introduced, the position of the arc is regulated by a solenoid while it is possible to watch the operation through mica plates in the front and back walls. In the Moissan furnace the substances to be acted upon are poured into the furnace through a carbon tube heated by the arc. The melted substance falls into a hollowed hearth from which it can be drawn off. The Zerener apparatus is intended primarily as a welding or soldering instument but might easily be used in the laboratory as a blowpipe.

The highest temperature which can be reached with the arc is somewhere between 3500° and 4000°, the temperature at the cathode being about 2700° while that of the anode may run up to 3500°, the sublimation temperature of carbon. With metal electrodes no such temperature can be reached because the metals boil before this point is attained. *W. D. B.*

The Importance of Electrochemistry in Organic Chemistry. *W. Löb. Zeit. Elektrochemie*, 3, *42* (*1896*). Kékulé believed that the action of alcohol on acids produced an anhydrid and then the ester. The author finds that a solution of phthalic acid in alcohol when electrolyzed gives an almost quantitative yield of phthalic anhydrid and later a quantitative yield of the ester. By the electrolysis of hydrogen sulfid in acetic acid, no sulfur is precipitated at the anode, while sulfo-acetic acid is formed, due to the action of acetic anhydrid on hydrogen sulfid. Several other illustrations are given of the usefulness of electrolysis in determining the organic reactions taking place under certain conditions. It is interesting to note that the reduction of nitrocompounds is credited almost entirely to the direct action of the metals and not to nascent hydrogen. The author's application of the dissociation theory is not yet in a form to be considered seriously. *W. D. B.*

On the Electrolysis of Salts of Organic Acids. *C. Schall. Zeit. Elektrochemie*, **3**, *83* (*1896*). From experiments on sulfo-acids the author concludes that the intermediate step in the change of alkyl carbonates into esters by electrolysis is the formation of an acid superoxid having the general formula $(RCO)_2O$. It will be remembered that Löb, Zeit. Elektrochemie, **3**, 42 (1896), assumes the intermediate formation of an acid anhydrid. *W. D. B.*

On the Toxic Action of Dissolved Salts and their Electrolytic Dissociation. *L. Kahlenberg and R. H. True. Bot. Gaz.* **22**, *81* (*1896*). The authors have studied the toxic action of a large number of electrolytes at different concentrations upon the seedlings of *Lupinus albus* L. The limiting concentration at which death no longer occurs is 1/6400 g-equiv. per liter for HCl, HBr, HNO_3, H_2SO_4 and $KHSO_4$, a result well in accordance with the dissociation theory. For KOH the limiting concentration is n/400; for $CuSO_4$, $CuCl_2$, $CuAc_2$, $FeSO_4$, $NiSO_4$, $Ni(NO_3)_2$, $CoSO_4$, $Co(NO_3)_2$, n/51200. It is known that addition of cane sugar and an alkali to a solution of a copper salt decreases the concentration of copper as ion and in one experiment under these conditions the authors found that death did not occur even in a n/400 solution of $CuSO_4$. Ferric chlorid is a powerful toxic agent, dialyzed iron a weak one. $Cd(NO_3)_2$ first becomes harmless at a dilution of 264800 liters. The toxic effect decreases as we pass from potassium cyanid to the ferrocyanid and ferricyanid. With $Hg(CN)_2$ apparently the two ions and the undissociated salt are all poisonous and the plants grow only when the dilution is 102400 liters. The limiting concentrations for Ag as ion is n/819200. The results with organic acids can not be classified since the anion has a toxic effect in many cases and the behavior of the sodium salts of these acids has not yet been studied. The authors are mistaken in believing that they are the first to state that the physiological action of a solution must be the sum of the effects due to the ions and the undissociated substance; see Dreser, Zeit. phys. Chem. **13**, 377 (1894). *W. D. B.*

Structure Phenomena

The Spectrum of Argon. *J. Trowbridge and T. W. Richards. Am. Jour. Sci.* [*4*] **3**, *15* (*1897*). 5000 storage cells of the Planté type were available in preliminary experiments with a Geissler tube of pure argon under pressure of about 1 mm. A resistance of several million ohms was usually interposed; and with about 2000 volts the red glow was readily obtained by the steady unidirectional current. With a condenser discharging between the terminals of the Geissler tube, the blue glow appeared, consisting of an intermittent discharge. The introduction (between Geissler tube and one plate of the condenser) either of a small coil having self-induction or of ohmic resistance, changes the color from blue to red, the oscillations being now damped or prolonged. A tube of argon may thus serve as an inductometer; the influence of self-induction and of ohmic resistance may be compared; and the proper working of a Hertz oscillator may be tested. The word «talantascope» is suggested for an argon tube fitted for the study of electrical waves.

A battery of 10000 cells is to be used in further studies, with more highly rarified gases, yielding Röntgen rays. *R. B. W.*

The Progress of Spectroscopy. *H. Kayser. Chem. Zeitung; Chem. News*, **74**, *307* (*1896*). An interesting review of spectroscopy, from which it appears that spectroscopy first became a real science on the introduction of the Rowland gratings. For, in the prism apparatus it was hardly possible to measure wave lengths in the visible spectrum to one ten-millionth of a mm, a defect far too great for accurate work. In the Rowland grating apparatus it is now possible to measure wave lengths to one ten-thousand-millionth of a mm. This great accuracy led to very important advances. Equations were deduced connecting groups of lines. Balmer has given the formula for the hydrogen spectrum.

$$\lambda = A \frac{n^2}{n^2-4}$$

where A is a constant $= 3647$ and n varies from 3 to 15. Kayser and Runge have shown that the spectra of several elements are given by the formula

$$\frac{1}{\lambda} = A + \frac{B}{n^2} + \frac{C}{n^4}$$

where A, B, C are constants different for each element and n the series of whole numbers from 3 upwards.

After a recent examination of cleveite gas Runge and Paschen have concluded that this gas consists of two elements, one of which is helium, the other unnamed. For «its lines can be arranged in six series, three of which consist of narrow double lines. Of these, two possess constant differences of vibration and terminate at the same place; the third which contains the strongest lines contains couples of a decreasing difference of vibration. The three series thus form conjointly a spectrum which exactly corresponds to the type of the alkalies; these are the two by-series and the main series». We find in the spectra of the alkali metals just such arrangement. Runge and Paschen draw the «certain» conclusion that the cleveite gas consists of two elements only, all the lines found being included in the six series.

The spectrum of argon has not yet been examined with sufficient accuracy to justify any positive statement of its nature. The author inclines to the view that it is a simple element. In mercury Eder and Valenta have found a hitherto unknown band spectrum which is interesting on account of the monatomic nature of mercury.

C. L. S.

New Examples of Normal Rotary Dispersion. *P. A. Guye and P. A. Melikian. Comptes rendus,* **123**, *1291* (*1896*). Data for thirteen organic compounds. *W. D. B.*

DISTILLATION WITH VAPOR

BY C. H. BENEDICT

If the vapor pressure of a substance at a given temperature is less than the external pressure, the substance will not boil at that temperature if a liquid, nor sublime if a solid. Since distillation by diffusion is too slow a process to appeal to anyone, it is necessary to reduce the external pressure until it equals that of the substance under consideration or to add a volatile substance in such quantity that the vapor pressure of the system is equal to the atmospheric pressure. The first method has been used by Ramsay and Young[1] to determine the vapor pressures of liquids and of solids. The second method is used very largely in purifying organic compounds. When the pressure of the system is made equal to the atmospheric pressure by addition of air, the process is spoken of as distillation with an air current. When the volatile component is water vapor we speak of distilling with steam. There are two cases to be distinguished in distilling with vapor; when the substance to be distilled is a liquid and when it is a solid. The first case presents no difficulty. In order to get the best yield the volatile component added should be a vapor which is not soluble in the liquid to be distilled. Under these circumstances the vapor pressure of the system is the sum of the pressures of the two pure components; and the same amount of the liquid to be distilled passes over per volume of vapor as if the distillation had been carried on with an air current or at the same temperature by means of diminished external pressure. If the vapor added dissolves freely in the liquid to be distilled, the partial pressure of the latter is reduced and the quantity of this component in the unit volume of vapor is less than if the other component was not present.

When the substance to be distilled is a solid at the temperature of the experiment, matters are very different. There is present the

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[1] Phil. Trans. **175**, 37 (1884).

monovariant system, solid, solution and vapor; and the question at once arises as to the concentration in the vapor phase of the substance to be distilled. Since the solid phase is in equilibrium with the vapor, Ostwald[1] says that the partial pressure of the solid component in the vapor phase must be equal to the vapor pressure of that component in the pure state; but Bancroft[2] has shown that this is not necessary theoretically.

Margueritte-Delacharlonnay[3] has found that strong solutions of sodium hydrate, sodium carbonate and ferric sulfate yield vapors at 60–70° in which the presence of the solute can easily be detected. It is always possible that some of the solution is carried off mechanically, especially since McLeod has shown that a tube filled with glass beads is not sufficient to remove potassium chlorid carried over mechanically by the oxygen formed from potassium chlorate.[4] In this case the amount of solid salt was so great that it could be detected optically in the gas. On the other hand the evaporation from a strong solution at 60–70° is not so rapid as to cause an enormous amount of liquid to be carried off in the vapor and it is therefore safe to say that Margueritte-Delacharlonnay has called attention to a phenomenon which is worthy of careful study. Very recently much the same result has been obtained by Bailey.[5] He investigated the volatility of some alkaline chlorids in presence of water. From a triple-normal solution there distilled some forty-three milligrams of cesium chlorid per liter of water. While the vapor pressure of cesium chlorid has not been determined, there can be little question that this result is much in excess of what was to be expected and it should also be kept in mind that the solution was not saturated.

Gooch's experiments on the volatility of boric acid are still more remarkable.[6] He found that boric acid distilled much more rapidly when heated with a given volume of methyl alcohol than

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[1] Analytische Chemie, 33; Cf also Wildermann. Zeit. phys. Chem. **11**, 407 (1893) and Nernst. Theor. Chem. 376.

[2] Jour. Phys. Chem. **1**, 147 (1896).

[3] Comptes rendus **103**, 1128 (1886).

[4] Jour. Chem. Soc. **69**, 1015 (1896).

[5] Ibid. **65**, 445 (1894).

[6] Proc. Am. Acad. **22**, 167 (1886).

with the same volume of water. Since a given volume of water furnishes a larger volume of vapor than an equal volume of methyl alcohol and boils at a higher temperature it should be doubly effective for the distillation of boric acid whereas the reverse is the case experimentally. This volatility of boric acid is often accounted for in an off-hand manner by assuming the formation of a volatile, instable ester. I am not aware that any experimental evidence has been offered in behalf of these curious hypothetical compounds and it does not seem probable that any will be forthcoming. While boric acid might easily form an ester with methyl alcohol, such a compound with acetone needs justification and yet boric acid distills readily with acetone. A much simpler explanation would be that of an increased vapor pressure of the solute due to the nature of the solvent.

Villard[1] finds that iodin is soluble in carbonic acid vapor and Hannay has shown that salts are distinctly soluble in vapors near the critical temperature and pressure while Rose[2] has found that gold volatilizes much more rapidly in an atmosphere of carbon monoxid than in one of coal gas and that its volatility is increased by the presence of copper or platinum. From these facts it seems safe to conclude that the nature of the solvent has an effect on the partial pressure of the solute even when the latter is present in the solid form and it becomes desirable to test this conclusion experimentally. To this end a few measurements on the volatility of naphthalene in the presence of ether have been made. These determinations are only first approximations and will be repeated with more care in this laboratory during the coming winter.

An excess of the solid was always present so that the solution might not become supersaturated. An ordinary 250 cc distilling flask was used. The distillate was analyzed by evaporating to dryness at room temperature with an air current. There are two sources of error here. The solvent may not be entirely driven off and some of the solid may evaporate. Luckily these two errors are in opposite directions and counterbalance each other to some extent. A test

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[1] Comptes rendus **120**, 182 (1895).

[2] Jour. Chem. Soc. **63**, 714 (1893).

experiment with a known solution of naphthalene in ether showed that this method of analysis was accurate to about two percent.

Two different distillations of naphthalene and ether gave for the composition of the distillate 1.181 grams of naphthalene to 13.06 grams of ether and 1.404 grams of naphthalene to 16.4 grams of ether. From these data it is possible to calculate the possible pressure of each component provided we assume that the variations from the Gas Theorems are of the same order and sign for the two components. If x and y denote the number of reacting weights of the two components in any quantity of vapor and the barometer stands at z mm of mercury, the partial pressures will be $xz/x+y$ and $yz/x+y$ millimeters of mercury because the vapor pressure of the system at the boiling point is equal to the external pressure. Taking 128 as the reacting weight of naphthalene, 74 as that of ether and 760 mm for the height of barometer, the above data give for the partial pressure of naphthalene 37.7 and 36.0 mm of mercury. A variation of the barometer of 30 mm would produce a change of less than four percent so that no serious error is introduced here. It remains to be seen what temperature this refers to and whether the result is too high or too low. The system, solid naphthalene, naphthalene in ether and vapor, must have a constant boiling point so long as the external pressure remains unchanged. This temperature is about 62°. There were some fluctuations owing to there being nothing in the flask to ensure steady boiling ; but this may be neglected. On the other hand the vapor began to condense before it passed through the side tube and the temperature at this point was of course much lower since the vapor is chiefly ether. A thermometer in the vapor stood at about 40°. It is however only at the surface of the liquid that the pressure of the system is equal to the external pressure. The temperature there is the one which must be taken. This great temperature difference could be eliminated by having the side arm of the distilling flask close to the surface of the liquid. This was deliberately avoided in the present set of measurements because it increased the liability of the solution being spattered over which would have vitiated the experiment. Also, the partial condensation of the vapor decreases the amount of naphthalene in the vapor and therefore if the distillate is more concentrated than one would expect from the vapor pressure of naphthalene, one could be certain that the real difference was even greater. The conditions of the experiment tend to make the quantity of naphthalene in the distillate less than in the vapor. On the other hand any loss of ether through evaporization would tend to reverse this. This loss was made as small as possible by surrounding the receiver with ice. The value 37 mm is to be considered as the provisional partial pressure of naphthalene at a temperature of 62°. There may easily be an error of twenty percent in this determination. This is of no importance since the vapor pressure of pure naphthalene at its melting point, 79.2°, has been found to be 9 mm by Naumann[1] and this value has been accepted by Ramsay and Young.[2] There is therefore an enormous increase in the volatility of naphthalene due to the presence of ether.[3] Distillation with an ether current would give not less than four times as much naphthalene as if the process were carried on with an air current or under diminished external pressure. With alcohol or benzene it is impossible to make measurements under atmospheric pressure because naphthalene is miscible in all proportions with either of these liquids before the boiling point is reached.

Some rough measurements with camphor in different solvents gave similar results, the amount of camphor in the distillate being in excess of that calculated from the vapor pressure determinations; but the great solubility of camphor in organic solvents makes this substance a difficult one to work with so that these results are not yet in a state suitable for publication. There seems to be no question, however, that the solvent does affect the vapor pressure of the solute and this opens up a new field of research, for the relation between the amount of this effect and the nature of the solvent has to be determined. The most plausible assumption would be that

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[1] Ber. chem. Ges. Berlin, 4, 74 (1871).

[2] Phil. Trans. 175, 44 (1884).

[3] The great difficulty experienced by all chemists in trying to purify gases from impurities which are ‹‹carried over mechanically›› is a strong argument in favor of the view that there may be something more than a ‹‹mechanical mixture›› in the vapor phase.

the more soluble the substance is in the liquid, the more soluble it is in the vapor. This is only an assumption and lacks experimental confirmation as yet.

It should be remembered that if we consider the liquid and gaseous states as passing continuously one into the other, the solubility of a substance in a vapor is a necessary consequence. Some day we shall have solubility curves for solids in vapors as well as in liquids. While the difficulties of measurement will be much greater in the former case than in the latter, we shall have much more opportunity to study mass action than is now possible. The concentration of the solvent vapor can be varied from zero up to that in equilibrium with the saturated solution whereas a change of pressure has very little effect on the concentration of the liquid solution phase.

This research has been carried on under the direction of Professor Bancroft in the chemical laboratory of Cornell University.

July 1, 1896.

A TRIANGULAR DIAGRAM

BY WILDER D. BANCROFT

It is a very simple matter to express graphically the changes in composition of a given phase with the temperature when there are only two components; but a concentration-temperature diagram presents great difficulties when the number of components equals three. The problem has been solved in quite a number of ways as has been pointed out by Roozeboom.[1] Most of the methods give a solid figure, the temperature being taken as the vertical axis; but it is possible to tell a great deal from the projections of the curves for the monovariant systems upon a plane, even though the temperature can no longer be read directly. Schreinemakers[2] takes for the X and Y axes the amounts of two of the components in a constant quantity of the third. This is open to the objection that there is no place in the diagram for an anhydrous double salt, nor for solutions containing very little of the third component. Meyerhoffer[3] has invented a diagram which has the merit of allowing one to take the temperature as one of the co-ordinates. In a system composed of two salts and water, he measures the ratio of one salt to the other along one axis and the temperature along the other. This is serviceable in certain cases; but is very limited in application since it neglects the relative quantities of both salts in respect to the third component. The method proposed by van Rijn van Alkemade[4] seems to have no advantage over the diagram of Schreinemakers. Gibbs[5] has suggested the use of a triangular diagram, the sum of the components being kept constant. If we take an equilateral triangle of unit height, the corners of the triangle will represent the pure components and any point within the triangle will represent some definite mixture of the three substances. The amount of each component

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[1] Zeit. phys. Chem. **12**, 367 (1893).

[2] Ibid. **9**, 67 (1892).

[3] Ibid. **5**, 97 (1890).

[4] Ibid. **11**, 306 (1893).

[5] Trans. Conn. Acad. **3**, 176 (1876).

is given by the length of the perpendicular from the point to the side opposite the vertex corresponding to that component. This diagram has been used by Thurston[1] in some work on alloys and was also suggested independently by Stokes[2]. Roozeboom[3] has used a modification of this diagram. He takes the isosceles right-angle triangle, the equal sides being of unit length. The advantage of this arrangement is that one can use the ordinary co-ordinate paper; but it is open to the objection that there is a different scale along the hypotenuse from that along the sides, so that one of the components seems to occupy an exceptional position. While this is not serious in the case of two salts and water where the water is solvent and the salts solutes, it is a disadvantage in the ternary systems in which no such distinction exists and becomes impossible when the system of three components is considered as a subdivision of one containing four.

Roozeboom[4] has proposed another form of triangular diagram which is distinctly superior to either of those already considered. It consists of an equilateral triangle with lines ruled parallel to each side instead of perpendicular to them. The length of one side is taken equal to unity and the same scale is used for the binary systems in the sides of the triangle as for the ternary systems in the interior. It has seemed to me worth while to act upon this suggestion of Roozeboom and I have had made triangular co-ordinate paper with lines ruled parallel to the three sides. Since there are some interesting geometrical relations connected with the use of this diagram, only a few of which have been mentioned by Roozeboom, I propose to give a brief sketch of the information which can be read off directly from Figure 1.

We will suppose that we have the components, A, B and C and that the sum of these components always equals 100. The choice of units is entirely arbitrary but must be adhered to when made. The corners of the diagram marked A, B and C represent phases

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[1] Proc. Am. Acad. **26**, 114 (1877).
[2] Proc. Roy. Soc. **49**, 174 (1891).
[3] Zeit. phys. Chem. **12**, 369, (1893).
[4] Zeit. phys. Chem. **15**, 143 (1894).

containing one hundred percent of the components A, B and C respectively. The composition of any phase containing A and B only will be represented by a point on the line AB; while phases containing only A and C or only B and C will be found on the lines AC and BC respectively. Any phase containing all three components will be represented by some point in the interior of the diagram. The composition corresponding to the point O can be read off in a number of different ways. Through O draw lines parallel to each of the three sides. The usual way of determining the composition is to start from one corner as the origin and measure along the two sides. Thus AX measures the amount of C, AY the amount of B in the unit mass of the phase, while the amount of A is given by the difference. In this particular case the co-ordinates of the point O are A = 40, B = 50, C = 10. Sometimes it is desirable to read

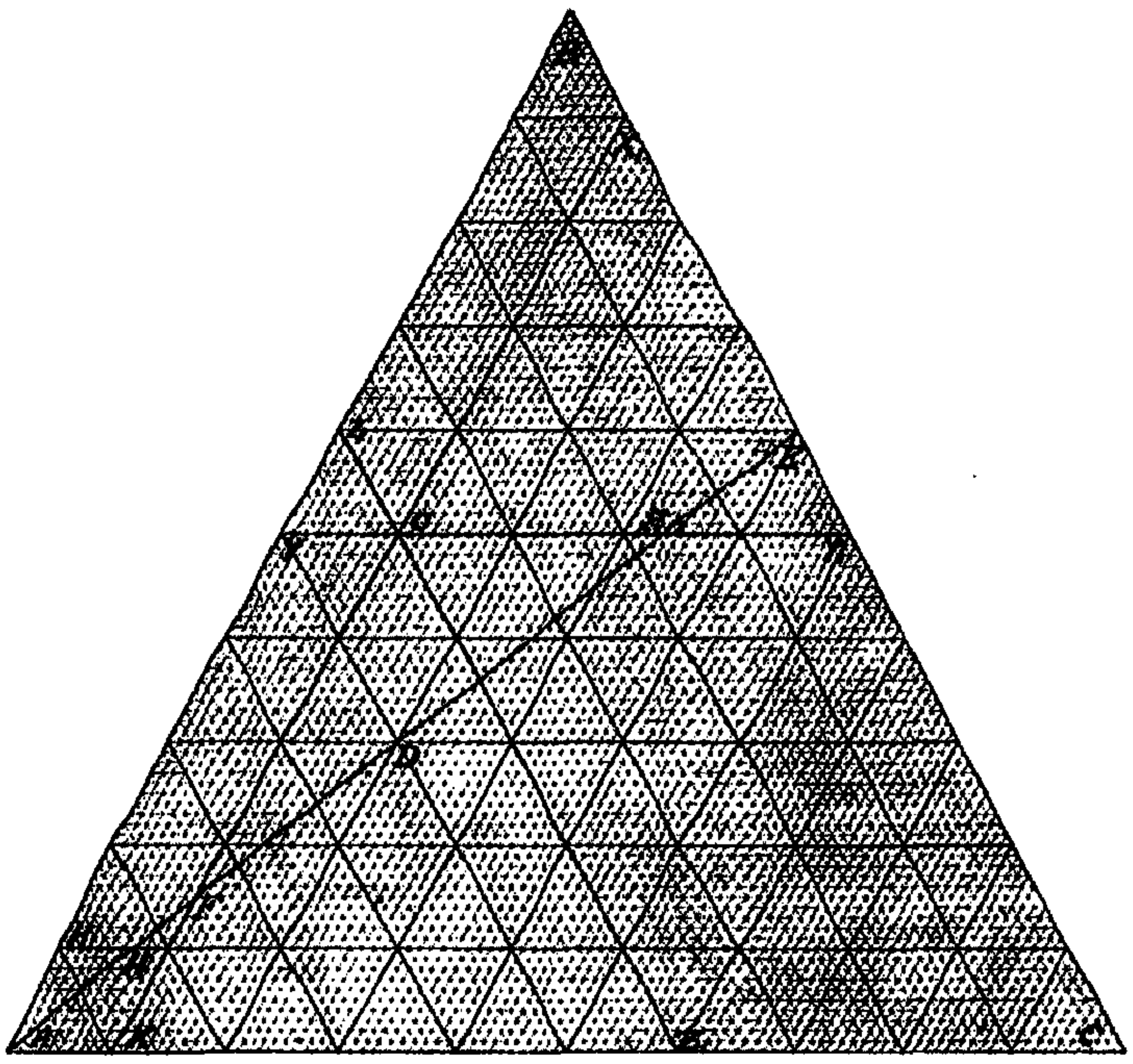

FIG 1.

off the value from one side only, let us say the side AB. AY is a measure of B, YZ of C and BZ of A. This will easily be seen to be true for OY = YZ by construction, being sides of an equilateral triangle. AX = YO since they are opposite sides of a parallelogram. BZ is the remainder of the line AB and therefore is a measure of the quantity of A in the unit mass of the phase. The same process can be carried out for all three sides of the diagram if desired. The lines BZ, OX_1, OY_1, X_1Y_1 and CZ_1 are all equal and measure A; the lines AY, OX, OZ_1, XZ_1 and CY_1 are all measures of the component B while AX, OY, OZ, YZ and BX_1 perform the same function for C. This may be summed up into the following general rule for determining parts of each component in the mixture: Lines being extended from O parallel to the sides, the interior sect gives the value for the opposite component and each external sect that for the component at the opposite end. It may not be amiss to mention that the concentration A = 40, B = 50, C = 10, would be represented by the same point O if the co-ordinate paper were made with lines perpendicular to the sides instead of parallel to them.

Besides knowing the amounts of A, B and C in one hundred parts of A + B + C, it is sometimes desirable to determine the quantity of B in one hundred parts of B + C, for instance. This is also given by the diagram. Let us suppose a phase having the composition A = 50, B = 30, C = 20. This phase will be represented by the point D. Draw a line from the corner A through D. The line AD cuts BC at E. The distance CE gives the amount of B in one hundred parts of B + C; in this case CE = 60. BE will therefore give the amount of C in one hundred parts of B + C. The line AD cuts the line denoting a 10 percent concentration of B at H and ten times the distance HH_1 or 66.7 is the amount of C in one hundred parts of B. In the same way ten times the distance FX gives the parts of B in one hundred parts of C. If the multiplication of the distance by ten seems to introduce too large an error, one can take the point at which the line AD cuts the line for 20 percent or 50 percent concentration of one component and then the distance is multiplied by five or two respectively. Thus twice H_2Y is equal to ten times HH_1 and gives the parts of C in one hundred parts of B. The line for 50 percent of C in the ternary solution cuts AD outside the diagram. To determine the corresponding relation between A and B or A and C we have only to draw the line CD or BD and proceed as before.

If one wish to present simultaneously the behavior of three components, or any part of them or each one separately this can be done by a very slight modification of the diagram. In Fig. 2 are given what few data there are for the system made up of potassium, sodium and lead nitrates.[1] In the central triangular diagram the lines meeting at O represent the three monovariant systems containing two solid phases, solution and vapor. Perpendicular to each side of the triangle are the temperature axes and the curves which are given there are the concentration-temperature diagrams for the three binary systems. The curves for potassium and lead nitrates do not reach

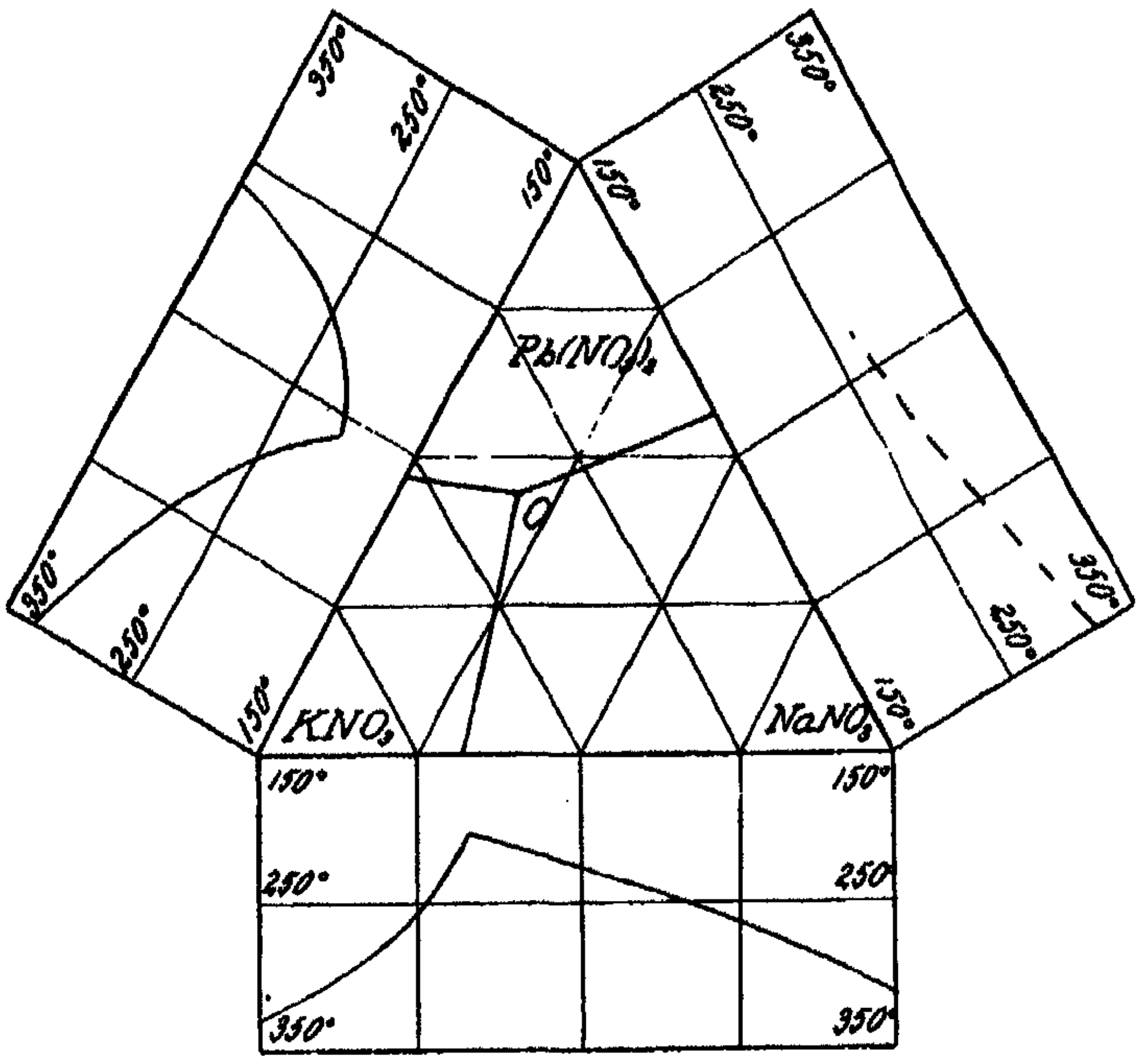

FIG. 2.

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[1] Guthrie, Phil. Mag. [5] **17**, 472 (1884).

the point corresponding to one hundred percent of lead nitrate because this substance decomposes before its melting point is reached. Only two points are known for the system, lead and sodium nitrates, the melting point of sodium nitrate and the composition and melting point of the eutectic alloy. For this reason only one branch of the curve is given and that in a dotted line. It would be possible to have the temperature axes follow the lines of the co-ordinate paper, making angles of sixty and one hundred and twenty degrees with the sides of the triangle. The objection to this is that one branch of the curve for the binary system is crowded together while the other is drawn out giving a very distorted effect. In each corner of the figure it is possible to draw a line perpendicular to one of the temperature axes and present the pressure-temperature diagram for each of the single components. This has not been done because the vapor pressures of the three salts have never been determined.

Returning to the concentration-temperature diagrams for the different binary systems, there are one or two points yet to be considered. The curves in these diagrams represent graphically the temperatures of the points along the sides of the central triangle. If we wish to learn the temperature of any point on any side of the inner triangle we have only to erect a perpendicular from the point to the concentration-temperature curve for the binary system and read off the temperature at the point of intersection. This can best be seen perhaps if we consider the complete diagram for a ternary system. As has already been stated, this forms a solid figure with the temperature as vertical axis. If now we imagine the three concentration-temperature diagrams for the binary systems revolved ninety degrees on the sides of the central triangle as axes we shall have the shell of the solid figure just referred to and the curves in the rotated diagrams are the outside upper edges of the complete model for a ternary system. The method of representation adopted here shows the temperatures of points along the sides of the triangle upon which the actual model is projected, but it does not give any information as yet in regard to the temperatures in the interior of the triangle. The usual way of doing this is to draw isothermal lines; but this obscures the diagram by multiplying the number of lines. In many cases it will therefore be of advantage to represent these temperatures in the side diagrams of the binary systems. This can be done by a series of lines each giving the relation between temperature and concentration when two components vary and the third remains constant. The curves already drawn in the side diagrams are for one hundred parts of two of the components and zero parts of the third. The succeeding curves would represent systems containing one hundred parts of two components and ten, twenty, thirty, etc., parts of the third substance. To determine what concentration this refers to in the triangular diagram where the sum of the three components is always one hundred, it is only necessary to drop a perpendicular to the side of the triangle and draw a line from there to the opposite vertex. The point at which this line cuts the line for ten, twenty or thirty percent concentration of the third component represents the desired composition.

While it is not possible to represent the compositions and temperatures of any phase in a ternary system by single points in a plane, it is possible to do this if one uses two points for each determination. This method has been employed by van der Heide in his study of the system, potassium, and magnesium sulfates, and water.[1] He expresses the concentrations in parts of each component per hundred parts of the solution. The temperature is taken as one axis while the concentration of the two salts are laid off on the other axis right and left from a zero point. Under these circumstances there are are two points for each nonvariant system and two curves for each monovariant system. This method has very great advantages. The temperature corresponding to each concentration is given directly and one can determine from the diagram the accuracy or inaccuracy of Meyerhoffer's theorem that the sudden change of direction of the solubility curve in passing through the inversion temperature does not affect the solubility of the solid phase which remains. In addition to the behavior of the binary systems, that of each of the salts with water can easily be shown, as indeed van der Heide has pointed out. The objection to be made to the diagram in its present form is that the concentration of the third component, water, can not be measured directly; but has to be obtained by a process of addition and subtraction and also that solutions contain-

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[1] Zeit. phys. Chem. **12**, 416 (1893).

ing only two salts can not be represented by a single line. This could be avoided by a very slight modification, measuring the temperature along the ordinates. Let the abscissas be a line of definite length corresponding to one hundred parts of the solution. Lay off the concentration of one component from the extreme left of this line and the concentration of the second from the extreme right. The concentration of the third component is given by the distance between these points. The binary systems can then be represented in the same diagram by single lines since one of the lines for the ternary system coincides with one of the Y axes when either the first or second component disappears while the two lines coalesce if it is the third component which vanishes.

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CUPROUS CHLORID

BY J. K. HAYWOOD

Lescoeur[1] has shown that when cuprous chlorid is treated with water, there is formed cuprous oxid and hydrochloric acid. He also found that when freshly precipitated cuprous chlorid is washed with water, the amount of acid in the wash water remains practically constant after the first few times until all the cuprous chlorid has been converted into the oxid. In Table I are given Lescoeur's data, under A being the number of the washing and under B the concentration of hydrochloric acid in the wash-water expressed in grams per liter.

TABLE I

A	B	A	B	A	B	A	B
1	1.580	4	0.132	12	0.132	20	0.139
2	0.212	8	0.137	14	0.133	30	0.011
3	0.139	10	0.136	16	0.129	34	0.000

Lescoeur offers no explanation of these rather curious results but it seems as if there could be no doubt about the cause of the phenomenon. The system contains three components and as soon as cuprous oxid is formed there are four phases, cuprous chlorid and oxid, solution and vapor. At a given temperature there can only be one concentration—in this case *n*/270—for which the system is in equilibrium. As long as there is an excess of hydrochloric acid there will be no cuprous oxid and the system will be a divariant one, capable of existing at different concentrations for a given temperature. This is exactly what Lescoeur found. This seemed to be such an interesting case of equilibrium that I repeated the measurements in a thermostat so as to be certain that the temperature did not vary. I placed some freshly precipitated cuprous chlorid in

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[1] Am. chim. phys. (7) 2, 97 (1894).

a flask containing water. The bottle was carefully stoppered and placed in a thermostat kept at 30°. At the end of about twenty minutes most of the solution was poured off and ten cubic centimeters were titrated with caustic potash. The flask was filled with water and replaced in the thermostat and the same series of operations was repeated half a dozen times. The results are given in Table II. The values given are the number of cubic centimeters of a one-hundredth normal caustic potash solution necessary to neutralize ten cubic centimeters of the hydrochloric acid solution.

TABLE II

(1)	42.13	(3)	8.73	(5)	11.0	(7)	12
(2)	8.75	(4)	8.78	(6)	13.1	(8)	11

In the first measurement there was an excess of hydrochloric acid and no cuprous oxid so that the difference between the first and the second measurement is normal. Measurements 2–8 do not agree among themselves as they should. Thinking that the system might not have reached equilibrium, I let another lot stand an hour and a half and found that 10.7 c.c. KOH were necessary to neutralize the acid. I then made measurements every fifteen minutes pipetting off ten cubic centimeters without refilling the flask. The readings thus obtained were 14.7, 20.8, 27.2, 35.8, 45.2, 57.4 c.c. showing that equilibrium had not been reached. I then made measurements at intervals of forty minutes exactly, decanting the whole of the solution as far as possible and refilling the flask with water. The readings were now 9.6, 9.3, 9.2, 9.3, 9.5 c.c. showing that it was possible to get constant values when the time-intervals and the relative masses of the reacting substances do not vary. It seems very certain from my measurements that Lescoeur's results were purely accidental and due to his having consciously or unconsciously used always about the same amount of wash-water and having made his measurements with surprising regularity.

Since the measurements do not refer to a system of equilibrium, it was to be expected that the relative masses of the different phases would have an effect. In order to test this I took three flasks, A, B and C, with approximately the same amount of cuprous chlorid in each but with 60, 30 and 15 c.c. of water respectively. Making determinations every fifteen minutes and changing the water between each reading, I obtained the results which are given in Table III.

TABLE III

A	B	C
6.3	6.8	13.7
6.1	6.3	14.1
5.5	6.0	13.9
6.0	6.5	

The reaction velocity changes very rapidly as we pass from fifteen to thirty cubic centimeters of water and then seems to change very little, if at all.

I made one attempt to determine the equilibrium concentration when cuprous chlorid and cuprous oxid are present as solid phases; but the result was not satisfactory owing to the action of the air dissolved in the water on the cuprous chlorid and the extraordinary length of time necessary to reach equilibrium.

Cornell University : January, 1896.

TWO LIQUID PHASES

FIRST PAPER

BY WILDER D. BANCROFT

Roozeboom[1] has already pointed out the different types of equilibrium to be expected in three-component systems with only one liquid phase; but he has not discussed the possibilities when two liquid phases can coexist. The object of this paper is to go over qualitatively some of the ground not yet covered by Roozeboom. Let us suppose that we start with three substances, A, B and C, which form no compounds; that the melting point of A is higher than that of B; and that A and B can form the binary nonvariant system, solid A, two solutions and vapor. This system has no degrees of freedom; but on adding the third component C, there is added a degree of freedom and the four phases, solid A, two solutions and vapor can exist over a range of temperatures, terminated only by the appearance of a new phase or the disappearance of an old one.

In all the two-component systems, which have yet been studied, the inversion temperature for the quadruple point, solid, two solutions and vapor lies between the temperatures at which the pure components melt. It will, nevertheless, be convenient to distinguish three types which may be represented by phenol and water, naphthalene and water benzene and water. In the first, the inversion temperature is only about two degrees[2] above the freezing point of water while it is a good deal below the melting point of phenol. In the second the inversion temperature is but little lower than the melting point of naphthalene and, relatively speaking, far above that of ice[3]. With benzene and water the melting points are only a

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[1] Zeit. phys. Chem. **12**, 367 (1893).

[2] Alexejew Wied. Ann. **28**, 332 (1886).

[3] On determining this point myself, I found that water lowers the freezing point of naphthalene less than a degree instead of six degrees as I had been told was the case.

few degrees apart and the inversion temperature is therefore not very far from either, though very much nearer the temperature for benzene than for water. There is no fundamental difference between these three types but certain equilibria are easier to realize in one case than in another. For instance with phenol and water it is very difficult to find a third component which will give a quintuple point at temperatures near the melting point of phenol while with naphthalene and water, it is very difficult to have ice in equilibrium with two solution phases and vapor when the third component is not a liquid at the temperature of the experiment.

Whether the temperature of the three-component nonvariant system, two solids, two solutions and vapor, be higher or lower than the inversion temperature for the two-component nonvariant system, solid, two solutions and vapor, depends primarily upon the relative solubility of the third component in the other two. If we call phenol A, water B and the third component C, we can make the following classification :

I. The component C is a solid at all temperatures included in the experiment.
  a. C is soluble in B, practically insoluble in A.
  b. C is soluble in A, practically insoluble in B.
  c. C is soluble in A and B.
II. The component C is a liquid at all temperatures included in the experiment.
  a. C is consolute with liquid B, practically nonmiscible with liquid A.
  b. C is consolute with liquid A, practically nonmiscible with liquid B.
  c. C is consolute with both liquid A and liquid B.
III. The component C is a gas at all temperatures included in the experiment.
  a. C is much more soluble in B than in A.
  b. C is much more soluble in A than in B.
  c. C is readily soluble both in A and in B.

Ia. The component is a solid, soluble in water, insoluble in phenol. Potassium nitrate and sugar satisfy these conditions. The effect of adding C is to decrease the mutual solubilities of the two substances A and B. Since the solution in which A is solvent becomes more and more dilute with addition of C, the monovariant system, solid phenol, two solutions and vapor, can exist at higher and higher temperature the more of C is added. The final nonvariant system will have A and C as solid phases. Since potassium nitrate is not very soluble in cold water, it will precipitate before the temperature has risen very much, while with sugar the temperature difference between the inversion point for the ternary system and that for the binary system shall be much greater. This is the case experimentally. The temperature at which solid phenol separates from a mixture of phenol and water forming two liquid layers was found to be + 0.8° when using ordinary phenol. On adding potassium nitrate in excess, the temperature was raised to over + 2° while with sugar a temperature of ten degrees was reached without difficulty and the solution was not yet saturated with sugar. With the increasing nonmiscibility of phenol and water caused by adding potassium nitrate, sugar or any substance coming under the heading Ia, one of the solutions can be made to approach pure liquid phenol in composition to within almost any degree of accuracy depending on the solubility of the component C. Since the temperature at which this solution phase can be in equilibrium with solid phenol can not be forced above the melting point for pure phenol, solid solutions being excluded, it follows that no matter how soluble in water the third component may be, a quintuple point with two solution phases is always possible, that the temperature at which this point occurs can never be higher than the melting point of pure phenol and that the solid phases are necessarily phenol and the third component. Since the maximum rise of temperature which is possible with phenol and water is nearly forty degrees and with naphthalene and water less than one degree, it is clear that the absolute rise of temperature on adding a given quantity of potassium nitrate will be much less for the monovariant system with naphthalene as component A than for the one with phenol.

Ib. The component C is a solid, soluble in phenol, insoluble in water. Naphthalene will serve as an instance. The effect of adding the component C will be to make the two liquids A and B less miscible than they are ordinarily. The difference between the behavior of sugar and the behavior of naphthalene is that with the former we approach a saturated solution of sugar in water and a phase composed of pure liquid phenol as limits while with the latter we approach a saturated solution of naphthalene in pure phenol and a phase composed of pure water as limits. In the first case the solution in which phenol is solvent becomes dilute and the solution in which water is solvent becomes more concentrated with increased addition of sugar while in the second case the solution in which water is solvent becomes more dilute and the solution in which phenol is solvent more concentrated with increased addition of naphthalene. The temperature at which solid phenol can exist in equilibrium with two solutions and vapor will be raised by addition of sugar and lowered by addition of naphthalene. If the component C is only sparingly soluble in phenol, it will precipitate as solid phase before the temperature reaches the freezing point of water and we shall have the nonvariant system, phenol, solid C, two solutions and vapor. This system can not be formed with naphthalene but it could probably be realized if sulfur were taken as the third component.

If naphthalene be added continuously to a mixture of phenol and water the temperature at which solid phenol can coexist with the two solutions and vapor will soon fall below zero. Since the phase in which water is solvent is continually becoming more dilute, it is clear that at some temperature not far below zero degrees we shall have ice separating and the formation of the nonvariant system, phenol, ice, two solutions and vapor. If we continue to add naphthalene keeping the system at constant temperature the phenol will melt and finally disappear, the concentrations remaining unchanged. With increasing concentration of naphthalene in the solution in which phenol is solvent, the solution in which water is solvent will disappear. When this has vanished, leaving the divariant system, ice, solution of water and naphthalene—principally the latter—in phenol and vapor, a further addition of naphthalene will cause the formation of the monovariant system, ice, naphthalene, solution and vapor. On raising the temperature there will come a point at which the ice begins to melt with formation of a second liquid layer and we have the nonvariant system, ice, naphthalene, two solutions and vapor. The temperature of this quintuple point is necessarily higher than that of the one in which phenol replaces naphthalene as solid phase because there is more naphthalene in solution and therefore the phase in which water is solvent is more dilute and can coexist with ice at a higher temperature. Using crude phenol the temperature for the quintuple point with naphthalene as solid phase was found to be about — 0.8° while with phenol as solid phase the temperature was several tenths of a degree lower. These measurements are only approximate and will be repeated using pure phenol.

Changing from the particular to the general, we may make the following statement: If the component C is sparingly soluble in A, the solid phases in equilibrium with two solutions and vapor will be A and C. If C is sufficiently soluble in A, two quintuple points of the type under consideration will be possible, the solid phases being A and B in the one case, B and C in the other.

The temperature of the quintuple point with A and B as solid phases is lower than that of the one with B and C as solid phases. It is to be noticed that the difference between these two temperatures will be greater the more soluble A and B are and the greater the difference in the concentrations of the solutions in which A is solvent for the two cases that A and that C is the solid phase.

Ic. The component C is a solid, soluble both in phenol and in water. Pyrogallol would undoubtedly come under this head though I know of no experiments with it. The effect of adding the component C is to increase the mutual solubilities of the components A and B. This solvent effect is not very large in most cases and is usually neglected in applications of Nernst's Distribution Law. Since both solutions become more concentrated the temperatures are lowered at which solid phenol and ice can appear. If the concentration in the solution in which water is solvent increases faster than the concentration in which phenol is solvent, the only solid phases which can exist in equilibrium with two solutions and vapor are phenol and the third component. If the concentration in the solution in which phenol is solvent increases faster than the concentration in the other solution we shall have much the same behavior as with substances classified under Ib. There will either be one quintuple point with phenol and the third component as solid phases or there will be two quintuple points with phenol and ice in the one case and ice and the third component in the other. There is one important difference however. In case there are two inversion points, the one with A and B as solid phases will exist at a higher temperature than the one with B and C as solid phases whereas the reverse was the case when C was insoluble in B. It may also happen that the solubility of the third component in the other two and its solvent action may be so great that the two solutions will become consolute before a second solid phase appears. This will be realized if we take glycerol as the third component.

In classifying these three cases, Ia, Ib and Ic, it has seemed easiest to consider the third component as insoluble in one or the other of the two components A and B or as soluble in both ; but this can not be defended as exact since all solids are somewhat soluble in all liquids according to the view generally adopted. This discussion has brought out the sense in which the classsification is to be taken. We group under Ia all solids which precipitate A from the solution in which B is solvent, under Ib all solids which precipitate B from the solution in which A is solvent and under Ic all solids which increase the mutual solubilities of A and B.

IIa. The component C is a liquid, miscible in all proportions with water and practically nonmiscible with melted phenol. I am not able to name such a substance ; but its effect will be similar to that of the component C in Ia and the temperature, at which phenol can exist in equilibrium with two solutions and vapor, will rise with increasing addition of the component C. Since this third component can not form a solid phase by definition, no quintuple point is possible.

IIb. The component C is a liquid, miscible in all proportions with liquid phenol and practically nonmiscible with water. Chloroform would come in this category. The addition of chloroform will lower the freezing point of phenol and the nonvariant system will have phenol and ice as solid phases.

IIc. The component C is a liquid consolute both with liquid A and liquid B. Alcohol or acetone may be taken as typical instances. Addition of alcohol or acetone will bring the two solutions nearer in composition and will also lower the temperature at which phenol can exist as solid phase. There are two possibilities. The freezing point of the phenol may be lowered so much more rapidly than that of the water that the ice may appear as solid phase before the two solutions become identical in composition, forming the nonvariant system, phenol, ice, two solutions and vapor. If that is not the case, one of the solution phases will disappear leaving the divariant system, phenol, solution and vapor. The condition for the first state of things is that the concentration of the third component shall be much larger in the phase in which phenol is solvent than in the phase in which water is solvent while the condition for the second case is the reverse of this.

IIIa. The component C is a gas, much more soluble in water than in phenol. Hydrochloric acid answers this description. The effect of adding the component C will be the same as in Ia and IIa, namely that the miscibility of A and B decreases and solid A will be stable at higher and higher temperatures. It was found experimentally that, using the ordinary hydrochloric acid of the laboratory, solid phenol appeared at twenty-five degrees above zero. Since hydrochloric acid can not separate as a solid phase there is no nonvariant system possible with two solution phases.

IIIb. The component C is a gas, much more soluble in phenol than in water. This could undoubtedly be realized with some organic compound though there are no data upon the subject. The freezing point of the phenol will be lowered by the addition of the component C and the solid phases at the quintuple point will be phenol and ice.

IIIc. The component C is a gas, readily soluble both in A and in B. The effect will be the same as in IIc, a lowering of the freezing point of phenol and either no inversion point with two solution phases in equilibrium or one with phenol and ice as solid phases.

The system, phenol, water and a third component, is typical of all systems in which the components A and B form the nonvariant system, solid A, two solutions and vapor; but, as has already been said, the relative positions of the quadruple point and the melting points of the components A and B determine the ease with which theoretically possible quintuple points can be realized experimentally and affect the stoichiometric relations very markedly. If we add sugar to naphthalene and water we shall get the nonvariant system, naphthalene, sugar, two solutions and vapor, existing at a higher temperature than the binary nonvariant system for naphthalene and water; but the rise of temperature will be only a fraction of a degree. The maximum rise of temperature theoretically possible with a solid, soluble in water and insoluble in naphthalene is less than one degree while, with the corresponding case for water and phenol, a rise of nearly forty degrees may occur—at any rate on paper. With water and benzene the rise would be practically imperceptible. The molecular raising of the freezing point is thus a function of this temperature difference as has been pointed out by Nernst.[1] On the other hand adding a solid, soluble in melted naphthalene and insoluble in water will lead practically invariably to the quintuple point with naphthalene and the third component whereas with phenol and water the corresponding inversion point can be realized only in case the third component is very sparingly soluble in phenol. Benzene and water occupy an intermediate position since it is not difficult to find organic substances which will lower the freezing point of benzene less than six degrees nor to find others which will lower it more than that amount. Whether it is possible to lower the freezing point of naphthalene enough to give the two quintuple points with ice and naphthalene, ice and the third component as solid phases when the third component melts above 80°, is difficult to say. With sulfur one can not get below 70° and with phenanthrene[2] the temperature of the quintuple point would be about 48°. When the third component is a liquid at all temperatures covered by the experiment it is possible to have naphthalene and ice as solid phases. This could be realized with chloroform for instance; but it is very doubtful whether we should be justified in classifying the quintuple point, naphthalene, ice, two solutions and vapor under IIb. That would be calling naphthalene A, water B and chloroform C whereas it is much more probable that it should be classified under Ia, calling water A, chloroform B and naphthalene C. The point upon which the matter turns is whether naphthalene or chloroform is solvent at this temperature. If a mixture of naphthalene and

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[1] Zeit. phys. Chem. 6, 27 (1890).

[2] Miolati Zeit. phys. Chem. 9, 649 (1892)

chloroform at zero degrees, saturated with respect to naphthalene, lies on the fusion curve for naphthalene, the three-component system falls under IIb; if it is a portion of the solubility curve we must classify under Ia.

With phenol, water and glycerol it is probable that the two liquid layers would become consolute before ice appeared as solid phase; with benzene, water and glycerol this would certainly be the case; with naphthalene and water it would probably be impossible to find a solid which would not precipitate before the two liquid layers became of the same composition.[1] With liquids miscible in all proportions with water and with liquid naphthalene, the result will always be disappearance of the second liquid phase and formation of the divariant system, naphthalene, solution and vapor. With benzene and water, this is no longer the necessary result and with phenol and water, it is more likely to be the exception than the rule. Benzene, water and alcohol furnish the quintuple point, benzene, ice, two solutions and vapor. I have not tried other liquids.

It will be noticed that the direction in which the equilibrium is displaced on adding the third component is the same whether that component is a solid or liquid or a gas at the temperature of the experiment. This is a necessary consequence of the discovery by Raoult that, in a binary system, the change of the partial pressure is not a function of the physical state of the pure solute at that temperature and of the conclusion of van 't Hoff that for many purposes the solute may be considered as if it were present in the gaseous state in the volume occupied by the solution. This view does not involve the further assumption that the components in a solution necessarily behave in all ways like gases though this is often overlooked. In certain ways a solute may be expected to behave like a liquid and to show a solvent or a precipitating action, depending on its nature and on that of the other components. This is seen to be the case in the systems which have been discussed in this paper. Since the solvent action of a liquid mass is a function of its chemical nature, it is to be expected that in the cases where the solute is to be treated as a liquid we should get a specific effect for each solute and the con-

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[1] It might be worth while to try pyrogallol.

centration would not be the only factor in the problem. This is an experimental fact since it has been shown that benzene precipitates water to different extents, varying with the nature of the consolute liquid[1] or, putting it the other way round, ethyl alcohol does not change the mutual solubilities of benzene and water in the same way that methyl alcohol or acetone does.

Nernst[2] has called attention to the fact that a mixture of ether, water and a third substance, soluble in ether and insoluble in water, gives a more constant freezing point than is the case with binary monovariant systems. The explanation which he offers for this apparent anomaly is a very simple one. The concentrations of the ether and of the third component in the aqueous phase and consequently the temperature at which ice is formed, depend upon the concentration of the third component in the ethereal phase. Since the amount of ether and of the third component in the aqueous phase is very small, the change in the concentration of the ethereal phase, with increasing separation of ice, will be negligible in most cases and the temperature will remain practically constant until this aqueous phase disappears. It is clear from this that the monovariant system, solid A, two solutions and vapor will behave in one way on withdrawal of heat if the the third component is soluble in the component A, insoluble in B and in a very different way if the third component is soluble in B and insoluble in A. To take a concrete case, we may suppose a mixture of naphthalene and water to which a little pheuanthrene has been added. Solid naphthalene begins to appear, let us say, at 78°. As naphthalene separates, the concentration of the solution in which naphthalene is solvent increases and the freezing point falls. Before the phase in which naphthalene is solvent disappears, the temperature will fall in the neighborhood of thirty degrees. An analogous case to the one described by Nernst would be found with phenol, water and hydrochloric acid. Here, as the phehol separates the amount of water which passes into the other solution phase will not be sufficient to change the concentration to any extent and the

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[1] Bancroft. Phys. Rev 3, 21 (1895).

[2] Zeit. phys. Chem. 6, 30 (1890).

freezing point will remain practically constant. This will not be the case if the mass of the phase in which phenol is solvent is very large relatively to that of the phase in which water is solvent. Under these circumstances the freezing point would change as the phenol separated in solid form, the amount of the change being determined by the difference between the initial and final concentrations of the phase in which water is solvent.

It seems as though phenol might be a good substance to use in standardizing hydrochloric acid. It would merely be necessary to make a table once for all showing the relation between the concentration of hydrochloric acid and the freezing point of phenol and the actual determination of any particular acid would not take five minutes. If one read the thermometer to hundredths of a degree there should be no difficulty in determining the concentration of hydrchloric acid to within three hundredths of a gram per liter. Using the Beckmann apparatus still greater accuracy could be obtained; but there is little advantage in that. This would do away with all weighings and the difficulties accompanying the preparation of standard solutions and it is therefore to be hoped that some one directly interested in analytical chemistry will make the preliminary measurements necessary to drawing up a standard table.

Before we can get an accurate understanding of the behavior of ternary systems where two liquid phases are possible, it will be necessary to consider the relation between temperature and concentration for the divariant systems, two solutions and vapor, and solid, solution and vapor; the graphical representation of the various equilibria and the form of the isotherms. In addition there are the systems illustrated by potassium chlorid, acetone and water in which there can be two liquid phases at temperatures at which no two of the components form two liquid phases. The time at my disposal does not permit of my treating these points now and I shall have to postpone a consideration of them and take them up in a subsequent paper.

In this paper I have considered the general case of quintuple points with two solid phases, two liquid phases and vapor formed by adding a component C to two components A and B such that there can be formed the quadruple point, solid A, two solutions and vapor. The general results are:

1. The component C dissolves in B with precipitation of A. The freezing point rises. The solid phases at the quintuple point are A and C or else no nonvariant system with two liquid phases is possible.

2. The component C dissolves in A with precipitation of B. The freezing point falls. There is one quintuple point with A and C as solid phases or two with A and B, B and C as solid phases or one with A and B as solid phases.

3. The component C increases the miscibility of A and B. The freezing point falls. There is one quintuple point with A and C as solid phases or one with A and B as solid phases or there is formed the divariant system, solid A, solution and vapor.

4. If the component C dissolves in A with precipitation of B and there are two quintuple points, the one with B and C as solid phases will exist at a higher temperature than the one with A and B as solid phases.

5. If the component C increases the miscibility of A and B and there are two quintuple points, the one with B and C as solid phases exists at a lower temperature than the one with A and B as solid phases.

6. A convenient method has been suggested for standardizing hydrochloric acid.

Cornell University.

NEW BOOKS

Traité elémentaire de Mécanique chimique, fondée sur la Thermodynamique. *P. Duhem. Tome I. Large 8vo, viii and 299 pages. A. Hermann ; Paris. Price 10 francs.* The new treatise on chemical thermodynamics, by Duhem, is unquestionably one of the most notable publications of the year. It would be difficult to name any one who is better qualified to give a connected and well rounded treatment of the subject than is the famous theoretical physicist of the Bordeaux university. His book is planned for two volumes, of which the first is now issued : it supplies an introductory account of the analytical methods employed in the work ; an exposition of the general principles of thermodynamics, especially in their relation to chemical processes; and a study of false equilibria, velocities of change, and explosions. Detailed study of the phenomena of chemical equilibrium and of electrochemistry are presumably reserved for the succeeding volume.

To those who find pleasure in simple, clear and exact treatment of a subject, with orderly arrangement, lucid writing and beautiful mathematical form evident throughout, the present volume will bring peculiar gratification ; in the ways of literary, of mathematical and of scientific style it is preeminent among its kind, it is fairly to be regarded as the best extant exposition of the subject which it treats. The notation is everywhere well chosen, so as to be easily borne in mind, and the author always makes clear upon what assumptions his mathematical developments rest. These assumptions, moreover, the necessary working hypotheses of the theory, are always of a rational and controllable kind,—it may be assumed, for example, that there always exist actions capable of maintaining any realizable state, or that when a system is defined by its ‹normal› variables the heat capacity of the system is positive, but never that supposed molecules are smooth, elastic spheres nor any other rubbish of this fancy sort ;

our author is ever careful to keep down out of the sky and to confine himself to matters of immediate human interest.

Another peculiarity, which fortunately is likewise becoming a modern scientific fashion, lies in maintaining a broad view of the subject by keeping its historical development in the foreground ; and we find here an impartial judgment, none too common in France, of the worth of work done by other than French investigators. The book is down to date in this respect, too, such results as those of Witkowski on the specific heat of air and those of the author himself on viscosity and false equilibria being properly considered.

Until now it has not been a light task to gain a clear view of mathematical chemistry as a branch of science ; to do this has required such long study of the journal literature as only a specialist can give, and no one knows better than he the labor entailed in reading the extended series of the original and critical articles of our present author alone in this field ; but now that Duhem has assumed the task of organizing the entire subject into a compact and well arranged whole it can almost be said that he who runs may read. It is not to be doubted that this aid to the comprehension of what is known and how it is known will act as a powerful stimulus to the further development of the subject. And it may be added that the neglect of absolute rigor, amusingly deplored by Duhem in his preface, has pretty certainly increased the readability and the usefulness of his work.

The main treatment of the volume is prefaced by a delightful account, in about thirty pages, of the analytical methods and the simple principles of mechanics, which are used in the book ; this is something so far in character above the occasional introduction to calculus methods that the reader falls in love with the book at once,—a more useful fore-word can hardly be imagined. Eleven chapters devoted to chemical thermodynamics in general then follow, and the volume is concluded by the first section of its detailed applications,—relating to false equilibria and explosions. The general thermodynamics concern the energy law and thermochemistry, the entropy law and the general equations of thermodynamics, an interpolated chapter on the inevitable ideal gases, and an extensive study of the various types of reversible displacement of chemical equilibria. In the remaining four chapters, on false equilibria and explosions and occupying about one-third of the volume, appears an admirable digest of the content of the author's *Théorie thermodynamique de la Viscosité, etc.*, which was reviewed in this Journal, 1, 369. This part of the work is thoroughly original and new and, as has been before remarked, is a most interesting discussion of the subject of turbulent actions; the successive chapters concern viscosity and friction, false equilibria and the ‹point of reaction›, the velocities of reactions, and explosions. That the velocities of change should appear, as they very naturally do, in connection with these things is most interesting.

The publisher's share in the work is, on the whole, commendable; the pages are large and the text and equations are well arranged, all of which adds materially to the comfort and pleasure of reading. The type, however, is not of the best, it is not for example to be compared with the graceful forms with which Gauthier-Villars has printed most of the author's previous work. Still, this is a minor matter and is offset by the low price at which the book is offered. The lack of subject and author indices will, it is hoped, be made up in the second volume. The book, as a whole, supplies an admirable account of modern exact physical chemistry, and every scientific library, as well as every person at all interested in the present status of chemical theory, should have a copy of it.

J. E. Trevor

Commercial Organic Analysis; *a Treatise, etc. Alfred H. Allen. Second Edition, Revised and Enlarged. Vol. III, Part 3. 507 pages. P. Blakiston, Son & Co., Philadelphia, 1896. Price $4.50.* This installment of the well known Commercial Organic Analysis will probably meet with the same cordial reception from analytical chemists as that accorded to the previous volumes of this valuable work. The part now issued treats of the less important vegetable alkaloids, not already considered in volume III, part 2; the non-basic vegetable bitter principles; animal bases, including ptomaïnes; animal acids and cyanogen compounds. The whole of the subject matter has been carefully revised and considerably enlarged. The material has been taken from a great variety of sources and a large number of the methods have been investigated by the author himself. Not only is the latest and most reliable information always given but in many cases the experience of the author as well as the methods devised by him are given.

This volume together with its predecessors is absolutely indispensible for the analytical chemist. There is no other book like it. Perhaps it might be criticised because of its fullness for there is undoubtedly much material in this book, which one would naturally expect to find in special treatises on the subjects or in the chemical dictionaries. In regard to this, however, it is only fair to state that the author fully realized that this criticism might be made and says in his preface: «I am fully aware that much of the matter is scarcely such as might be expected to be contained in a work purporting to treat of commercial analysis, but I have thought it better to include all facts possessing for me an analytical or practical interest, believing that what I find useful myself will also be of value or interest to others».

Altogether the book is unique and invaluable of its kind and should be in the library of every chemist who is engaged in doing analytical work. *W. R. Orndorff*

Elektrochemische Uebungsaufgaben. *F. Oettel. Octavo, viii and 53 pages. W. Knapp, Halle, 1897. Price 3 marks.* This is a laboratory manual for teachers of electrochemistry and it contains the following chapters: Testing and calibration of instruments, relation between the potential difference at the electrodes and current density, concentration, temperature and distance between the electrodes; effect of current density and concentration on the course of electrochemical reactions; measurement of gases evolved as a means of following reactions; electrolysis with membrane; precipitation of metals, using soluble and insoluble anodes; introduction of secondary reactions; experiments with melted electrolytes; experiments with metallic partitions; organic syntheses. No experiments with electric furnaces are given since this part of the subject is to be treated separately at some future time. The book is an excellent one and its defects are only what is to be expected under the circumstances. It was to have been used at the Zürich Polytechnic School and it is intended rather for the technical student than for those interested primarily in pure science. The book would have been even more satisfactory if there had been a chapter on the determination of the electromotive forces of several typical cells and another on polarization phenomena. The student should have practice in determining migration velocities with soluble as well as with insoluble anodes. On page 37 attention should have been called to the importance of the electromotive force when metals are to be separated, instead of leaving it to be supposed that the current is the sole factor. These criticisms would cease to apply if the book were entitled «Electrolytic Experiments for Technical Students». *Wilder D. Bancroft*

Die Prinzipien der Waermelehre, *historisch-kritisch entwickelt. E. Mach. Large 8vo. viii and 472 pages. J. A. Barth; Leipzig, 1896. Price: paper 10 marks, bound 11 marks.* The object of Mach's book seems to be to present clearly the actual ideas which constitute the present theory of heat, to exhibit the mutual relations of its parts, and to show how it has come about that this theory has developed as it has. The undertaking is accordingly entirely similar to that of the author in his justly famous treatise on mechanics,—an exposition of fruitful ideas and their growth, and not a codification of archives nor a storehouse of interesting curiosities. This promising programme has been ably carried out, as must have been expected from the higher order of Mach's previous contributions to the philosophy of science. In the book are presented successively the topics of thermometry, heat-conduction, calorimetry and thermodynamics. The treatment of these things is everywhere clear and well balanced, and the development of the theoretical views which come into question is in every case stated in a thoroughly original and appreciative way. The volume is concluded by over a dozen essays and sketches of philosophical import and together constituting something like a psychological study of the methods of physical science. These articles are immensely interesting and important; especial attention should here be directed to the one on the relation between physical and chemical processes, where it is shown that possible «chemical potentials» must be discontinuous, in contrast with the continuous potentials of physics, and the ground of contrast is sought in the definite mass-relations of the former case.

Mach's treatment of the early history of the theory, say of the period preceding Gibbs, arouses only admiration, but the remainder of the book has by far neither the same completeness nor the same finish. Horstmann's practical application of thermodynamic method to chemical action is neglected, Massieu's characteristic functions, Helmholtz's theory of free energy and its applications, v. Oettingen's antithetic developments and the magnificent work of Gibbs are all but little more than cited. This is indefensible, especially since the author brings his treatment so far down into the present as to touch upon the recent discussion on ‹energetics›. Then, again, the assemblage of both new and reprinted phliosophical sketches at the close, instructive as these are, is very disconnected; the book as a whole is neither a collection of scientific papers nor a well-rounded critical treatise on its subject,—we get the impression that a splendid work, partially finished, has been dumped upon the market in company with the materials for its completion.

A lack of care in revision is rather prominent; it surprises the younger of us to read (page 300) that Rankine has «recently» published a paper, which appeared in 1853, and we note a consistent fault in the pretty uniform phonetic (from the German point of view) spelling of English words occurring in the text; examples are ‹communicatet›, ‹ewer› and ‹electricyty›. Other printer's errors are present also, and further evidence of haste in publication is the lack of subject and author indices, which would have greatly enhanced the value of the book. The dress is the usual satisfactory output of the publishers, but the accompanying portraits of Dalton, Black, Carnot, Joule, Clausius and Kelvin are abominable and had better have been omitted.

These objectionable matters relate, however, more to form and finish than to actual content; the writer is impelled to recommend the book heartily,—it is an important work by an unusually able man, and no one interested in the philosophy of science, whatever his special field may be, can afford to pass it by. *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 which bear upon any phase of Physical Chemistry.

General

Reply to Prof. Boltzmann. *E. Zermelo. Wied. Ann.* **59**, *793 (1896).* In extending Maxwell's application of the theory of probability to the kinetic theory of gases, Boltzmann finds that the more the distribution of velocity in a system of molecules is removed from that denoted by the term «Maxwell's State» the quicker will be the change to that state, which once attained will be persisted in for an exceedingly (but not indefinitely) long period. He deduces a function H, which to a certain extent serves as a measure of the degree of variation from «Maxwell's State», and illustrates his argument by reference to a curve with H and t (the time) as coordinates.

This function H Boltzmann sets forward as the mechanical analogy of the entropy function ; concedes that thereby the second principle of thermodynamics is reduced from a «law of nature» to a «mere probability»; but argues that though from this point of view all phenomena must be regarded as periodic in nature, and not in the strict sense irreversible, yet the probability of any return to an initial state in measurable time is so small as practically to amount to zero.

This H function of Boltzmann's has been the subject of lengthy correspondence in Nature, vol. **51** (1894–5). Its analogy with the entropy is attacked by Zermelo, Wied. Ann. **57**, 485 (1896). Boltzmann replied, Wied. Ann. **57**, 773 (1896), and in the present article Zermelo reiterates his criticism, briefly as follows:

I. All actually occurring processes are in the thermodynamic sense *irreversible*, while in the mechanical systems presumed by the kinetic theory all processes are reversible; hence a *strict* analogy is impossible. This point is conceded by Boltzmann in reducing the second principle to the rank of a law of probability.

II. The analogy between the entropy function and Boltzmann's function H could be perfect only if H kept constantly decreasing during all measurable periods of time; it is not sufficient that H should finally attain a low value.

III. Whenever a system undergoes change, Boltzmann is compelled to assume that the initial state was less probable than the final state; but as changes are continually going on in nature, it would thus appear that the «less probable» states are among the commonest met with. *W. L. M.*

Reply to Zermelo's Article «On the Mechanical Explanation of Irreversible Processes.» *L. Boltzmann. Wied. Ann.* **60**, *392* (*1897*). See foregoing review. The author briefly reasserts his position that the second principle of thermodynamics may be mechanically explained by the «naturally unprovable assumption» that the universe, or at least that large part of it in which we ourselves are included, has proceeded from and still remains in what, from the point of view of the theory of probability, must be termed a ‹very improbable state›. If then a smaller system of bodies, in the state in which they happen to be at the moment, is suddenly cut off from the remainder of the universe, it must be considered *ex hypothesi* as in an ‹improbable› state, which as long as the system in question remains isolated is continuously replaced by more and more ‹probable› states; this is the ‹mechanical explanation of irreversible processes›.

In attempting to arrive at specialized conceptions of the universe one of two assumptions may be made; either that the whole universe is at present in a ‹very improbable› state; or, secondly, that although the universe on the whole is in thermal equilibrium, there exist here and there relatively small districts—‹individual worlds›—of the dimensions of our sidereal sphere, which during the relatively short period of aeons are noticeably removed from a condition of thermal equilibrium. Some of these worlds, *e. g.* that in which we ourselves live, are at present passing from a less to a more ‹probable› state, just as many, on the other hand, from a more to a less. This seems to be the only way in which the thermal death of each individual world can be accounted for without assuming that the universe as a whole is passing from a less to a more ‹probable› state.

The author has repeatedly urged the necessity of clearly recognizing that the present conception of the ultimate particles of bodies as material points must in the future prove merely provisional. He has never denied the importance of the Carnot-Clausius principle as the simplest embodiment of the facts of the science, but insists that the mechanical analogy is likewise in full agreement with the observations; and is of the opinion that the best means to a symmetrical development of our conceptions is to study the consequences of both. *W. L. M.*

On the Indispensibility of the Atomistik in Natural Science. *L. Boltzmann. Sitzungsber. Akad. Wiss. Wien.* **105**, (*Nov.*) *1896*; *Wied. Ann.* **60**, *231* (*1897*). Images of physical fact are now furnished in two ways, by the atomic hypothesis and by representation of the facts by differential equations—the «mathematico-physical phenomenology». Both methods have great value; to assert that the latter is the superior is as harmfully dogmatic as the reverse statement has been. Boltzmann's present contention is that the atomic hypothesis retains peculiar advantages; that either method may develop so as finally to absorb the other; and that consequently both should, at least for the present, be developed together.

Both methods furnish thought-pictures of phenomena; to do this for a comprehensive field is really possible, while direct description is not; so one's care should be to make his picture as little arbitrary as possible and not, with Ostwald, to make none. Now, Fourier's equation, as a type, expresses 1, that in every small time each of numerous «elements» (‹atoms› in the most general sense) takes the mean of the temperatures which the surrounding elements had at its beginning; and 2, that the assumed number of space and time elements shall be increased until further increase does not affect the result. The differential equation expresses that a finite number of elements *must* first be imagined, he who denies this «does not see the wood for the trees »); on not first distinguishing the neighboring elements the necessary mathematical operations become impossible, without this the conception of limits loses meaning. Does not then the picture with a finite number of elementary bodies lie the closer to the facts? The matter is not simplified by assuming that no difference exists between the limiting values and the actual facts. [Is it not equally gratuitous and unnecessary to assume that such a difference does exist?] Boltzmann does not here avoid the corollary that one must also consider, and in like wise, vector atoms, time atoms, *etc.*

Assigning to the ‹atoms› the fewest properties necessary for the representation of each field of phenomena we obtain special atomic hypotheses. Phenomenology attempts to combine these representations into one picture; its result must be very complicated, because the corresponding differential equations do differ. Further, these equations relate to nearly stationary states and so fail for turbulent actions. The plan of the «energetic phenomenology» is to consider all that is common to all the fields. These things are integral principles, such as the energy and entropy laws, and analogies; but both are too general to supply more than a little of the sought coherence of the facts, and, too, the analogies do not apply in all details. The plan of the atomic hypothesis is to so amplify and vary the assigned properties of the atoms as to get a simultaneous representation of different fields of phenomena; this certainly supplies a simple and comprehensive thought-picture, as *e. g.* of mechanics, heat, crystallography, definite proportions, isomerism, chemical optics, *etc.*, where the phenomenology fails to do so. This hypothesis furnishes also indications concerning turbulent actions. Yet the assigned properties must always conform with the special images of the phenomenology, wherefor the latter must be carefully developed. Boltzmann here enthusiastically maintains the consequences of the mechanical theory of heat to accord in their finest shadings with the pulse beat of nature; he apparently prefers a qualitative picture which is comprehensive in scope, to particular methods which yield exact results.

To develop a theory, as comprehensive as the present atomic hypothesis, upon as clear and unassailable a basis as that of Fourier's theory of heat-conduction, would be ideal; whether this will be done through combination of the phenomenological equations or through adaptation of the present atomic hypothesis, or both, is as yet wholly undecided. Atomistic views have certainly hindered progress in their day; yet they should not be abandoned, and one must keep carefully apart the phenomenology of established results and the atomistic hypotheses serving to hold them together. Boltzmann advises, at the close, against using the too narrow term Volume Elements for the «elements» of his paper. *J. E. T.*

The Constants of Nature. *Part V. A Recalculation of the Atomic Weights. F. W. Clarke. Smithsonian Miscellaneous Collections, No. 1075*, **28** *(1897).* In a large octavo volume of three hundred and seventy pages the author has collected and discussed all the atomic weight determinations. Morley's value, 15.88, is taken as the most probable value for the ratio of oxygen and hydrogen. The treatise will, doubtless, prove very serviceable to those who are actively interested in the determination of combining weights.

W. D. B.

Who Introduced the Use of the Balance into Chemistry? *Dobbin. Chem. News*, **75**, *68 (1897).* The author maintains that the more or less quantitative experimentation of van Helmont and of Boyle vitiates the claim that the first employment of the balance, in investigating theoretical questions in chemistry, is due to Lavoisier.

J. E. T.

A New Stirrer. *H. Schultze. Ber. chem. Ges. Berlin*, **29**, *2883 (1896).* Two glass balls hang by stiff platinum-iridium wires to a ring at the end of a glass rod. When the rod revolves on its axis (turbine) the balls stand out at right angles; when at rest they hang down, and the stirrer can then be introduced into narrow necked flasks. *W. L. M.*

Note on an Improved Specific Gravity Bottle or Pyknometer. *E. R. Squibb. Jour. Am. Chem. Soc.* **19**, *111 (1897).* Description of an instrument in which the standard water volume can be measured at a series of temperatures, and in which the contained liquids can be brought without loss to room temperature for weighing. An accuracy to the sixth decimal place is claimed. *J. E. T.*

The Use of Aluminum for Condensers. *T. H. Norton. Jour. Am. Chem. Soc.* **19**, *153* (*1897*). Measurements, with organic substances and with steam, to show that, so far as purity of the product is concerned, aluminum is better than glass for condensers in about the same ratio as tin, while for lightness and thermal conductivity it is better. *J. E. T.*

Monovariant Systems

Certain Kinetic Considerations, which seem to have Connection with the Theory of Vaporization and of Allied Processes. *W. Voigt. Göttinger Nachrichten*, **1896**, *No. 4*. Supposed interaction of molecules introduces difficulties into the kinetic-molecular theory, which disappear in the two limiting cases in which the average distance apart of the molecules is either great or small as against the radius of their spheres of action—the cases of ‹ideal gases› and of ‹ideal liquids›. The author develops the theory for the latter case; this had been attempted by Jäger, Wien. Akad. Ber. **99**, 679 (1890), but the author disagrees with Jäger's fundamental assumptions.

Denoting by c the velocity which a molecule must exceed that it may leave the liquid, and by ρ_l and ρ_a the densities of liquid and of vapor, the author finds c^2 to have the order of magnitude of

$$\frac{4K}{\rho_l + \rho_a}$$

where K is the capillary pressure. He then shows that ρ_l/ρ_a must be a function of the temperature alone, derives a formula for the heat of vaporization, gives a proof that Maxwell's law of the distribution of velocities may be assumed for both of the phases, and arrives at a relation

$$log\ (\rho_l/\rho_a) = (c/G)^2, -$$

G being the most probable velocity. After discussing the relation of this theory to the formulas of Stefan and of Bakker, relating capillarity and vaporization, an equation

$$Q = \frac{1}{2} G^2 [(c/G)^2 + 1]$$

is derived for the heat of vaporization, it gives Q one-third too small for water. After introducing the vaporization formula of Clausius into the theory, the distribution of solute between two liquid layers is studied, yielding K and

$$\frac{1}{2} (p_i + p_a) \log (p/p_a)$$

as of the same order ; p_i and p_a are the two osmotic pressures. This gives $K = 1.6$ atm for succinic acid with ether and water. Transforming the formula to make it express the heat of absorption of a gas it is found to give values far below the actual ones. The case of several solutes is discussed, and it is concluded that two liquid layers yield a vapor which would be in equilibrium with either layer taken alone.

The whole paper, carefully worked out and clearly written, as it is, supplies an admirable illustration of the practical uselessness of the kinetic theory as a theory of facts. *J. E. T.*

On the Effect of Pressure in the Surrounding Gas on the Temperature of the Crater of an Electric Arc. *Correction of Results in Former Paper. W. E. Wilson and G. F. Fitzgerald. Astrophys. Jour.* **5**, *101* (*1897*). In earlier experiments to determine whether the temperature of the crater in the positive carbon varies with the temperature of the surrounding gas, nitrogen, the authors had concluded that the temperature is lowered through a direct cooling of the carbon. This they now show to be erroneous, the observed fall in radiation being due to absorption by nitrogen peroxid which is produced ; the same phenomenon appeared with air under pressure and even with their oxygen, which contained some nitrogen as an impurity. It was noted that nitrogen peroxid heated in a flask changes from reddish brown to golden yellow and the characteristic absorption bands thereupon nearly disappear. The authors do not mention the careful work of Richardson, Jour. Chem. Soc. **51**, 397 (1887) on this decomposition.

Further experiments were made with hydrogen and carbon dioxid ; trees of soot were produced in the former case, as if by electrolysis of the hydrocarbons present as impurities, in the latter case it was observed that sudden reduction of pressure produces some sort of fog in the gas. The final conclusion drawn is that the experiments do not suffice to prove the temperature to be directly influenced by the pressure. The reviewer is unable to see why more care should not have been taken to provide purer nitrogen, oxygen and hydrogen. *J. E. T.*

On Solid Solutions and Superfluous Comments, a Reply to Herr Bodländer. *G. Ciamician and F. Garelli. Zeit. phys. Chem.* **22**, *134* (*1897*). As the title implies, the tone of the reply is rather peevish. The authors make two points: that their results are not sufficiently accurate to warrant any conclusion being drawn from them and that it is discourteous for anyone to prove anything from data obtained by other people. It is not likely that the second proposition will find general acceptance whatever may be true about the first. *W. D. B.*

The Application of Cryoscopic Measurements to the Solution of Questions of Chemical Constitution. *F. Garelli. Ber. chem. Ges. Berlin*, **29**, *2972* (*1896*). As a result of the author's cryoscopic studies, this Journal **1**, 256 (1896), it has been shown that the formation of solid solutions is independent of the chemical character of the reacting substances and depends only on similarity in their structural formulas. Thus, *monocyclic* substances (pyrrol, pyrrolidin, pyridin, piperidin, thiophene, cyclopentadien, *etc.*) give ‹abnormal› depressions in benzene; *dicyclic* (dihydronaphthalene, quinolin, isoquinolin, tetrahydroquinolin, indol, indene, cumarone, *etc.*) normal in benzene, abnormal in naphthalene; *tricyclic* (carbazol, tetrahydrocarbazol, acridin, naphthoquinolin, florene, diphenylene oxid) normal in benzene and naphthalene, abnormal in phenanthrene; while substances of the diphenyl type (tetrahydrodipyridyls, dithienyls, *etc.*) are abnormal in diphenyl solution only. If the dissolved substance contain ‹side chains›, *etc.*, the cryoscopic anomalies are usually less noticeable or altogether absent, except when the solvent likewise contains side chains similar in nature and position.

The results of cryoscopic measurements may thus be employed to decide cases of disputed chemical constitution: for instance, nicotin and metanicotin, giving normal depressions in diphenyl can not be hydrodipyridyls; and the behavior of tropanin and granatanin (normal in benzene, abnormal in naphthalene) is to be considered as evidence of this dicyclic nature, and confirmation of the constitutional formulas given them by Merling. *W. L. M.*

Anilin and Dimethylanilin as Cryoscopic Solvents. *G. Ampola and C. Rimatori. Gazz. chim. Ital.* **27**, *I, 35, 51 (1897).* The constant for anilin is found to be 58.77, for dimethylanilin, 58. The authors studied the change of the constant with the concentration but without reaching any very definite conclusions. *W. D. B.*

On the Heats of Vaporization of Liquids at their Boiling-Points. Miss D. Marshall. *Phil. Mag.* [*5*] **43**, *27 (1897).* The paper is a continuation of a previous one, Phil. Mag. [5] **41**, 38 (1896), and is occupied mainly with the description of modifications, improvements and corrections of the method of the former paper.

E. B.

On the Two Optically Isomeric Methyl Mannosids. *E. Fischer and L. Beensch. Ber. chem. Ges. Berlin,* **29**, *2927 (1897).* The dextrorotary and laevorotary forms crystallize below 8° and the racemate above 15°. The inversion temperature lies between these two points. The reaction is especially interesting because the three solid phases are anhydrous.

$$l\text{-}C_7H_{14}O_6 + d\text{-}C_7H_{14}O_6 \rightleftarrows (C_7H_{14}O_6)_2$$

This is the second case of the sort known, Bauer having discovered a similar reaction with mercury and silver iodids. The authors mention the curious fact that a concentrated solution crystallizes much less rapidly in a vacuum exsiccator than when exposed to the air. It is to be hoped that the authors will make some freezing point determinations with mixtures of the optically active substances. The pure components melt at 193° and the racemate compound at 167°.

W. D. B.

The Vapor Pressure of the Different Compounds of Calcium Chlorid and Water. *W. Müller-Erzbach. Zeit. phys. Chem.* **21**, *545* (*1896*). Vapor pressure determinations for hydrated calcium chlorid made by determining the concentration of sulfuric acid which does not take water from nor yield water to the crystals. For the efflorescence of the hexahydrate, the values lie between those obtained by Roozeboom for the change to the α-modification and to the β-modification. The author was unable to prepare the labile form ; on the other hand he had no difficulty in determining the dissociation pressure of the hexahydrate at 40°, a temperature at which it can not exist. Hydrated calcium chlorid changes readily from a plastic mass to one with a hard chalky consistency. *W. D. B.*

Method for Measuring Vapor Pressures of Liquids. *Kelvin. Nature*, **55**, *273, 295* (*1897*). A differential method in which the two liquids are sucked up into barometer tubes by means of an air pump, the two vessels containing the liquids being afterwards connected by a capillary tube. The method involves the use of considerable amounts of the two liquids and an accurate knowledge of the densities at the temperature of the experiment. *W. D. B.*

On the Variation of the Fusion Temperature with the Pressure. *R. Demerliac. Comptes rendus*, **124**, *75* (*1897*). The thermodynamic formula for the change of the freezing point with the pressure holds absolutely for benzene, paratoluidin and naphthylamin between one and ten atmospheres pressure. The author has made measurements at pressures up to 330 atmospheres and finds that the curve with pressure and temperature as coordinates is hyperbolic and that dT/dp approaches zero for constant increments of the pressure. This result is contradicted by the experiments of Damien, and the latter's measurements have been repeated and made to conform.
W. D. B.

Decomposition of Metallic Sulfates by Hydrochloric Acid. *A. Colson. Comptes rendus*, **124**, *81* (*1897*). When hydrochloric acid gas acts upon lead sulfate or copper sulfate there is formed the monovariant system, lead sulfate, lead chlorid, solution and vapor or copper sulfate, copper chlorid, solution and vapor. The author has shown that in each case there is a definite pressure for each temperature. He has neglected to show that this is no longer the case if the original concentration of the hydrochloric acid gas is below a definite minimum value. *W. D. B.*

Divariant Systems

On the Continuity of Isothermal Transformation from the Liquid to the Gaseous State. *T. Preston. Phil. Mag.* [5] **42**, *231* (*1896*). In the well known isothermal curve suggested by Prof. James Thomson, which figures so largely in van der Waals's work on the continuity of the liquid and gaseous states, the middle part represents a condition of the substance in which increase of volume involves a corresponding *increase* of pressure, a condition usually regarded as unimaginable.

In a spongy mixture of liquid and small bubbles of gas, the author finds a conceivable state in which the extraordinary demands of this part of the curve are at all events partially satisfied ; if the volume (of the bubbles) be increased, the capillary forces at their surfaces—which assist the extreme pressures in reducing their volumes—will be weakened, and the external pressure must be correspondingly increased to restore equilibrium.

As the author himself points out, such a system is experimentally irrealizable, as any disparity in size amongst the bubbles would result in growth of the larger and disappearance of the smaller amongst them ; even if realizable the arrangement suggested could hardly be considered as a ‹continuous› passage from the liquid to the gaseous state ; the paper must however be regarded as an ingenious attempt to render conceivable an ‹unimaginable› situation. The statement on page 238, that the equality in area of the two loops formed by Thomson's curve with the horizontal (‹boiling point› line) depends on the principle of the conservation of energy, is surely a clerical error. *W. L. M.*

The Connection between the Laws of Boyle, Gay-Lussac, Joule, etc. *R. E. Baynes. Zeit. phys. Chem.* **21**, *556* (*1896*). Comment upon Bakker's reply (this Journal, **1**, 198) to the author's strictures. He now says that in no sense is any one of Bakker's five laws a consequence of any of the others, but all are immediate consequences of the assumed equation of condition $p(v-b)=RT$. When a body obeys the Boyle-van der Waals law the remaining four laws do not hold unless the function $f(T)$ has the form kT. *J. E. T.*

Boyle's Law at very Low Pressures. *William Sutherland. Phil. Mag.* (*5*) **43**, *11* (*1897*). Surface condensation on the walls of containing vessels is supposed to produce the apparent departure from Boyle's law. The author proposes to show that the effect of such condensation should not necessarily be more appreciable at low densities than at high ones. The departure is due to special circumstances and not to any general failure of the laws. In a previous paper «Thermal Transpiration and Radiometer Motion», Phil. Mag. [5] **42**, 389 (1896), $\log p/p_a = (6A\pi\rho_2/v_1^2) \log (z_a/z)$, (20), was deduced, where p is the pressure of a gas at a distance z from a surface of a solid, p_a the pressure at a distance z_a, $3Am_1m_2/r^4$ the attraction between a molecule of gas (m_1) and of solid (m_2) at a distance r, ρ_2 the density of solid, and v_1, the velocity of m_1. Equation (20) applies to a gas obeying Boyle's law approximately. This may be written $p/p_a = (z_a/z)^{\beta/k}$, (29), where $\beta = 6Am_1\pi\rho_2$ and $k = m_1v_1^2$. When this expression is applied to the layer of molecules nearest to the solid wall, we find the pressure there by assigning a value z_s to z such that the attraction on a continuous normal cylinder ending at z_s from the surface equals the attraction on the discontinuous molecules in that cylinder; thus z_s will probably not be much different from half the mean distance of a molecule from its immediate neighbors near the solid surface. The domain of a molecule near the surface is m_1/ρ_1. So z_s is nearly $(m_1/\rho_s)^{1/3}/2$. Then from Boyle's law, $\rho_s/\rho = [2z/(m_1/\rho_s)^{1/3}]^{\beta/k}$, (29*a*). This specifies the density at the surface when that at any distance z is known. In most cases ρ becomes practically constant when z exceeds a certain small value. Let ds be an element of surface; erect a normal cylinder of height z, starting at $z_s/2$ from the surface, and reaching to $z + z_s/2$; with these as limits of integration, the mass of the cylinder is $ds\int \rho dz = ds \int \rho_a(z_a/z)^{\beta/k} = ds \int \rho_a(z_a/z)^{\beta/k} dz = [ds/(1 - \beta/k)]\, [\rho z - z_s(\rho_s - \rho)/2]$, (30). When z ends in the main body of the gas where surface-action is negligible, $ds\rho z = dB$, where B is an element of volume. So the mass of the cylinder is $[\rho dB - dsz_s(\rho_s - \rho)/2]/(1 - \beta/k)$, and the total mass $M = [\rho B - sz_s(\rho_s - \rho)/2]/(1 - \beta/k)$, (31). The quantity β/k is supposed small in comparison with unity. Where surface is increased by filling vessel with porous material, powder or bodies like charcoal, an equation like (31) should be written for each interspace, and for the gas in the whole of the interspaces we can use (31) when ρ is changed to ρ_c, the average density at the center of the interspaces. As β/k is small, it follows from (31) that the surface term is always small compared to the volume term and therefore the equation for a mass of gas in a vessel partially occupied by powder or porous material is $M = \rho_f B_f + \rho_c B_c$, (32), where the subscript f refers to the free volume, and c to that in the interspaces. Putting (31) in the form $M = \rho B + M\beta/k - sz_1(\rho_1 - \rho)/2$, (33), we see that however much we may rarefy a gas the relative importance of the surface term can never exceed a certain small limiting amount. This is the opposite of the commonly accepted view.

The experimental evidence for and against the above view is somewhat meagre; nevertheless the author seems to make out a strong case for his side. *C. L. S.*

Our Present Knowledge of Argon, with a Partial Bibliography. *C. L. Parker. Jour. Am. Chem. Soc.* **19**, *124* (*1897*). A review of the literature of the subject, with about five pages of closely printed bibliography. *J. E. T.*

On the Density of Ozone. *M. Otto. Comptes rendus,* **124**, *78* (*1897*). From the weights of a given volume of oxygen and of the same volume of oxygen and ozone the density of ozone can be determined if the quantity of the ozone in the vessel be known. The value found is one and one-half times that of oxygen. *W. D. B*

On an Absolute Determination of the Expansion of Water. *M. Thiesen, K. Scheel and H. Diesselhorst. Wied. Ann.* **60**, *340* (*1897*). Very careful determinations of the densities and specific volumes of water for a series of temperatures, varying by five degrees at a time from 0° to 40°C, on the international hydrogen scale. Unit density appears at 3.98°. Formulas for expressing the results are to follow. *J. E. T.*

Absorption. The Water in the Colloids, especially in the Colloids of Silicic Acid. *J. M. van Bemmelen. Zeit. anorg. Chem.* **13**, *233* (*1896*). The vapor pressure of a silicic acid jelly decreases with decreasing concentration of water to about 5 mm (at

15°). It remains nearly constant until the concentration has decreased a good deal and then changes again with further loss of water. The pressure-concentration curve thus consists of three parts, the middle one being nearly horizontal. So far this reminds one of Hoitsema's experiments upon the occlusion of hydrogen by palladium. The matter is further complicated by the middle portion not being strictly horizontal and by its occurring at slightly different pressures varying with the previous history of the jelly. Along this same portion, some new modification must appear because the first part of the curve is not reversible. The whole matter is very much more complicated than any one would have thought possible and it is hardly surprising that no satisfactory explanation of the phenomena is yet possible. *W. D. B.*

On the Solubility of Hydrated Mix Crystals. II. *W. Stortenbecker. Zeit. phys. Chem.* **22**, *60 (1897).* Determination of the isotherm at 18° for copper sulfate, zinc sulfate and water, a system giving three sets of solid solutions. Passing from solutions rich in zinc sulfate to those rich in copper sulfate the order of crystallization is rhombic crystals with seven of water, monoclinic crystals with seven of water and triclinic crystals with five of water. The ratio of copper to zinc is less in the rhombic crystals than in the solutions in equilibrium with them while the reverse is true with the other sets of crystals. Fractional evaporation of any solution will therefore yield rhombic and monoclinic crystals as final product. The curious fact was noticed that the crystals which first separate from a solution saturated with respect to the monoclinic salt are not really in equilibrium and take up more copper sulfate on standing. The author determined several states of labile equilibrium analyzing, among others, the solution in equilibrium with rhombic and triclinic crystals. *W. D. B.*

Contributions to the Knowledge of Isomorphous Mix Crystals. *Second Paper. H. Ambronn and M. LeBlanc. Zeit. phys. Chem.* **22**, *121 (1897).* The authors claim that all of Küster's reasons, Zeit. phys. Chem. **16**, 525 (1895), for objecting to their first paper are unsound; but they admit that his conclusion was right, even if reached in an improper way, and that isomorphous mix crystals are not to be likened to mechanical mixtures. *W. D. B.*

Polyvariant Systems

On the Slow Oxidation of Hydrogen and Carbon. II. *H. Hirtz and V. Meyer. Ber. chem. Ges. Berlin,* **29**, *2828 (1896).* With reference to their discovery that acid solutions of potassum permanganate absorb hydrogen, with evolution of an approximately equivalent volume of oxygen, this Journal **I**, 265 (1897), the authors point out that no ozone is liberated by the action of *dilute* sulfuric acid on potassium permanganate; further that *under the conditions of their experiments* manganese dioxid alone causes very little evolution of oxygen, see next review. Attempts to bring about the reverse reaction—absorption of oxygen by the products of the reaction of hydrogen on acid permanganate solution—gave negative results. *W. L. M.*

Reduction of Permanganic Acid by Manganese Dioxide. *H. N. Morse. Ber. chem. Ges. Berlin,* **30**, *48 (1897).* With reference to the work of V. Meyer on permanganic acid the author quotes from a paper, Morse, Hopkins and Walker, Am. Chem. Jour. **18**, 5 (1896), in which he has shown that permanganic acid is reduced by precipitated manganese dioxid with evolution of three-fifths of the (active oxygen) of the permanganic acid. This paper seems to have been sent off to the Berichte before the article by Hirtz and V. Meyer, see previous review, reached the author. *W. L. M.*

On the Combustion of Gases near Cooled Surfaces. *F. Haber and A. Weber. Ber. chem. Ges. Berlin,* **29**, *3000 (1896).* Experiments with Bunsen burners and with gas heaters by various makers. The amount of gas remaining unburnt (as high as 15 per cent in one case) depends almost entirely on the quantity of air mixed with the gas in the burner itself. In a Bunsen burner with proper access of air the gas wasted falls as low as 0.4 per cent. *W. L. M.*

On the Density and Mean Specific Heat between 0° and 100° of Alloys of Iron and Antimony. *J. Laborde, Jour. de Phys.* (3)

5, *547* (*1896*). Eight alloys were prepared by melting together in a crucible pure crystallized antimony and iron wire. The densities were almost all larger than that of iron (the denser element) showing contraction during solution. The mean specific heats were greater than if the mixture rule held. In both cases the maximum deviation from the mixture rule was for an alloy having approximately the composition Fe_2Sb_4. See this Journal **1**, *262*. *E. B.*

Osmotic Pressure

On the Determination of the Constants of Diffusion in Water of Several Gases. *G. Hüfner. Wied. Ann.* **60**, *134* (*1897*). The paper is mainly concerned with a method of avoiding convection currents by letting the gas diffuse *from below.* A glass tube of 8 mm to 14 mm diameter has its lower end closed by a «hydrophan» plate ½ mm thick. Such a plate will hold for weeks a pressure of from 2 to 3 cm of water. The gas is allowed to diffuse through the hydrophan plate, up through the water and out at the top. The dimensions of the apparatus and the rate of flow of the gas (in the steady state) permit the computation of the required diffusion constant. The results for CO_2, N_2O, O_2, N_2 and H_2 are compared with the values calculated from Stefan's work on CO_2. The agreement is satisfactory except for H_2, showing that the method can give good results. For H_2 no results agreeing with the theory could be obtained by this method. The author then tried the diffusion of H_2 in a long horizontal capillary tube. The result here was too large, the result by the other method being too small. For Cl_2 however this second method gave satisfactory results. The article closes with a table comparing the results obtained by the author with the values calculated on the basis of Stefan's measurements on CO_2. *E. B.*

On the Osmotic Pressure in Sprouting Seeds. *L. Maquenne. Comptes rendus*, **123**, *898* (*1896*). From the freezing points of the juices the author calculates that the osmotic pressures in seeds of certain peas and beans vary from five to ten atmospheres. He remarks that this would account for the fact that the seeds swell.

W. D. B.

Electromotive Forces

On Magnetism and Electromotive Force. *A. H. Bucherer. Wied. Ann.* **59**, *735* (*1896*). After translating some results of Duhem into formulas involving the vapor tensions of magnetized and non-magnetized iron—«the vapor of magnetized iron» is supposed to obey the ordinary gas laws—the author proceeds to build up an expression for the E.M.F. of a thermo-pair from the two hypotheses (*a*) that «the quantity of metal that participates in the change of heat to electrical energy bears a similar relation to the quantity of electricity transmitted, that the quantity of substance decomposed does in electrochemical phenomena,» and (*b*) that the work to be obtained from a given thermo-pair is equal to that obtainable by the passage of a «thermo-electrical equivalent» of the saturated vapor of the metals composing the pair, from the tensions corresponding to the hot junction to those corresponding to the cold.

The author seeks to connect his second hypothesis with the second principle of thermodynamics; he fails however to make clear in what sense the operations involving vapor transference and thermo-electric current respectively are to be considered as leading to the same end state. A comparison of theoretical results with experiment is not included in the paper. *W. L. M.*

On Two New Voltaic Cells. *H. Pauling. Zeit. Elektrochemie* **3**, *332* (*1897*). The first cell has carbon electrodes with sodium thiosulfate and chlorin as electrolytic fluids. This gives an electromotive force of about 0.5 V. (Sodium sulfite would work much better). The second cell has iron and carbon electrodes with ferric chlorid as electrolyte. The electromotive force is said to be 0.9 V. The cell is kept from depolarizing by renewing the solution continuously. The merit of the battery lies in the cheapness of the materials. The author estimates that with cells of this type nine hundred watt-hours would cost five cents. This is not based on any actual performance of the cell. *W. D. B.*

Experiments on Two Phenomena caused by the Passage of a Continuous Current through Organic Tissues. *G. Weiss. Jour. de Phys.* (*3*) **6**, *72* (*1897*). The maximum polarization in a frog's muscle is said to be about 0.2 V; with man it is higher and could not be determined owing to the pain caused by the current. When organic dyestuffs are dissolved in gelatine and the colored mass is placed in contact with colorless gelatine and electrolyzed, the color moves with the current if the dyestuff is basic and in the opposite direction if an acid. *W. D. B.*

Chemical Syntheses in the Ozone Apparatus. *S. M. Losanitsch and M. Z. Jovitschitsch. Ber. chem. Ges. Berlin*, **30**, *135* (*1897*). The authors passed various mixtures of gas through the ozone apparatus and in every case found chemical reactions to occur. The paper is preliminary, more exhaustive experiments are to follow. The gases experimented on so far are carbon monoxid, carbon dioxid, hydrogen, methane, ethylene, hydrogen sulfid, hydrochloric acid, ammonia, nitrogen and the vapors of benzene, water, and of carbon disulfid. *W. L. M.*

Electrolysis and Electrolytic Dissociation

The Electrolytic Dissociation Theory. *Armstrong, Lodge, Whetham, Herroun, Pickering, Rayleigh, Kelvin. Nature*, **55**, *78, 150, 151, 223, 253, 272* (*1896*). A series of letters on the dissociation theory started by Armstrong who remarks that while the theory of dilute solutions is broadly true in mathematical form, the fundamental premises on which it is based are destitute of common sense. The key note of the opposition is repeated by Pickering in the remark that a theory cannot be accepted unless it is reasonably probable, no matter what quantitative accuracy it may have. Under these circumstances discussion is useless. While the modern theory of solutions is not exact, it is the only theory which even attempts to give quantitative relations. There is no substitute offered. It is suggested that all the phenomena could be represented equally well by an association theory. This may be true but we have no association theory as yet. When it comes we can consider the relative merits of association and dissociation. It is perfectly legitimate to debate whether bread is better than cake; but the relative merits of half a loaf and no bread are already proverbial. *W. D. B.*

On the Relation of the Physical Properties of Aqueous Solutions to their State of Ionization. *J. C. MacGregor. Phil. Mag.* [*5*] **43**, *46, 99* (*1897*). The object of this paper is to test the applicability to sufficiently dilute solutions of an expression: $P = P_w + k(1 - \alpha)n + l\alpha n$ where P is the numerical value of any property, P_w that of the same property for water under the same physical conditions, n the concentration of the solute expressed in reacting weights per unit volume, α the dissociation coefficient and k and l constants which may be spoken of as ionization-constants and which will vary with the solvent, the solute, the property to which they apply, the temperature and the pressure, but not with the concentration of the solution. The author shows that the data for the density, thermal expansion, viscosity and refractive index of potassium chlorid and sodium chlorid solutions and of mixtures of these solutions can be represented by formulas of this general form. Since the agreement between observation and theory is satisfactory even for triple-normal solutions, it would seem that the author might have omitted the unpleasant restriction to «sufficiently dilute solutions». *W. D. B.*

A Satisfactory Method of Measuring Electrolytic Conductivity by means of Continuous Currents. *W. Stroud and J. B. Henderson. Phil. Mag.* [*5*] **43** (*1897*). Two arms of the Wheatstone's bridge through which the current flows in parallel have equal resistance. In the third arm is a resistance cell composed of a long capillary tube (30 cm) ending in test tubes with Pt electrodes. The fourth arm contains a similar cell with shorter capillary (4.9 cm), and the rheostat. This arrangement causes the polarizations to balance each other if equal. The tubes were calibrated by weighing their contents of mercury. This allows the computation of a constant which, if multiplied by the rheostat reading when the balance is obtained, gives at once the specific resistance of the liquid used. The polarizations usually balance within one percent. Using high E.M.F.s and high resistances makes the unbalanced residuum of no importance. Measurements were made on several KCl solutions and the results compared with those of Kohlrausch. The method is, in the opinion of the authors, more accurate and more convenient than Kohlrausch's method. The correctness of this opinion, especially as regards convenience, seems to the reviewer to be open to much doubt. *E. B.*

On Platinized Electrodes and Resistance Measurements. *F. Kohlrausch. Wied. Ann.* **60,** *315* (*1897*). A solution of 1 part platinum chlorid, 0.008 lead acetate and 30 water [solution of Lummer and Kurlbaum, Verh. phys. Ges. Berlin **14,** 56 (1895)] gives a platinized surface which is so effective as to permit the electrodes in Kohlrausch's method to be reduced very much in size. Electrodes of 0.5 cm^2 are sufficient for most purposes when platinized with the above solution. With electrodes of this size it is still possible to measure resistances as low as 20 ohms with an accuracy of 0.2 percent. A number of convenient forms of cell are described together with various methods and precautions relating to their use. *E. B.*

On Rheostat Plugs. *F. Kohlrausch. Wied. Ann.* **60,** *333* (*1897*). A comparison of resistance boxes with large and with small plugs shows that the small plugs are on the whole better. The resistance of a plug when properly set is about the same for large and for small plugs. Large plugs are more affected by the removal of neighboring plugs. Kerosene on a rag is good for cleaning the plug holes. The plugs should always be turned and not merely pressed in. *E. B.*

On the Electrolytic Conductivity of Solids. *C. Fritsch. Wied. Ann.* **60,** *300* (*1867*). Determinations of the conductivity of AgCl, AgBr, AgI, $PbCl_2$, $PbBr_2$, PbI_2, PbF_2, $HgCl_2$, $HgBr_2$, HgI_2, $CuBr_2$ and SiO_2, in the pure state and after addition of metallic oxids to SiO_2 and potassium or sodium salts to the other substances. In all cases the mixtures conducted better than the pure solids, though the increase is relatively small with silica. With rising temperature there is increasing conductivity. The author established no general relations between the increase in conductivity and the nature of the foreign substance added. This is not to be wondered at for he took no pains to determine whether the cases studied were comparable. With lead and potassium iodids there is undoubtedly a compound formed and also with the haloids of mercury and the alkali metals. Instead of distinguishing the three cases of no reaction between the salts, of formation of compounds and of formation of solid solutions, the author contents himself with the unwarrantable assumption that all mixture of solids may be considered as solid solutions. *W. D. B.*

Molecular Conductivity of Amidosulphonic Acid. *Joji Sakurai. Jour. Coll. Sci. Tokio*, 9, *II; Jour. Chem. Soc.* **69**, *1654 (1896)*. Amidosulfonic acid, NH_3SO_3, is of about the same strength as iodic acid and stronger than sulfurous acid. This is interesting because benzene sulfonic acid is stronger than any of the amidobenzene sulfonic acids. The migration velocity of the anion, HSO_3, is about 45.7. The change of the conductivity of sodium amidosulfonate with the concentration can be expressed fairly satisfactorily by van 't Hoff's modification of the Rudolphi formula. *W. D. B.*

A Contribution to the Study of Water Solutions of some of the Alums. *H. C. Jones and E. Mackay. Am. Chem. Jour.* **19**, *83 (1897)*. From conductivity and cryoscopic measurements the authors conclude that most of the alums exist to a certain extent as double salts in solution provided the solutions are not too dilute. While this result is not surprising in itself every convert to the study of concentrated solutions is to be welcomed. One very interesting point was brought out in connection with ammonium iron alum, that the hydrolytic action of water upon the solute is not finished as soon as the substance is dissolved. It is to be regretted that the authors did not attempt to study this as a case of reaction velocity, as was done by Sabatier for the action of water on metaphosphoric acid.
W. D. B.

On the Electrolytic Condition of Solutions in Methyl Alcohol. *G. Carrara. Zeit. phys. Chem.* **21**, *680 (1897)*. With reference to an article on the same subject by Zelinsky and Krapiwin, this Journal, **1**, 325 (1897), the author attracts attention to measurements of his own of the electrical conductivities of numerous substances in methyl alcohol. The measurements appeared in Gazzetta chimica Italiana, **24**, II, 504, and were reviewed Ber. chem. Ges. Berlin, **29**, R. 491 (1896), but appear to have been overlooked by Zelinsky and Krapiwin. *W. L. M.*

Separation of Metals by means of Soluble Anodes. *R. Pauli. Elektrochem. Zeit.* **3**, *180, 222 (1896)*. If we have the salts of two metals in solution and use the same two metals as electrodes, there will be practically complete precipitation of the metal which serves as cathode. This was tested successfully with the chlorids of antimony and iron. There must be a misprint in the value for the electromotive force of the cell. It is more likely to have been 0.2 — 0.3 V than ten times that amount. *W. D. B.*

Quantitative Determination of Manganese by Electrolysis. *Second Paper. C. Engels. Zeit. Elektrochemie,* 3, *286, 305* (*1897*). To a solution of potassium permanganate the author adds free acetic acid and hydrogen peroxid till the solution is decolorized. An excess of hydrogen peroxid is decomposed by chromic acid; chrome alum and ammonium acetate are added, and the solution is ready for electrolysis after nearly neutralizing with ammonia. The most favorable current density is 0.8—1.0 ampere. The author found that the nature of the precipitate varied with the potential difference used, being eighty-five percent manganese oxid and fifteen percent manganese peroxid in one case with 1.2 V and fifty percent manganese peroxid in another case with 1.5 V. Various experiments were made to determine the reason why presence of chrome alum is effective but no very satisfactory conclusion was reached. *W. D. B.*

On the Formation of Lead Sulfate in Alternating Current Electrolysis with Lead Electrodes. *S. Sheldon and M. B. Waterman. Phys. Rev.* 4, *324* (*1897*). Experiments on the formation of lead sulfate from lead electrodes in sulfuric acid. The amount of lead dissolved per coulomb increased with the current density, approaching, apparently, a limiting value. An increase of the frequency of the alternations increased the lead dissolved per coulomb until the rate reached 20 per second; after this there was a slow decrease. Experiments at 17°, 22° and 28° gave a temperature coefficient of — 0.0125 for the dissolved lead. No theory of the phenomena is presented. *E. B.*

Two Simple Electrochemical Lecture Experiments. *W. Nernst. Zeit. Elektrochemie,* 3, *308* (*1897*). A very dilute solution of potassium permanganate, to which a little urea has been added to increase the density, is placed in the bend of a U-tube. Both arms of the tube are filled with an equally dilute solution of potassium nitrate (0.003n) so carefully that the dividing surfaces are very sharp. When this system is electrolyzed under a potential difference of seventy volts the colored layer can be seen to move and the distance moved can be readily measured. In the second experiment mercury is allowed to drop in a coherent jet through a concentrated solution of a potassium or sodium salt. A platinum spiral is made the anode, the jet being cathode. The object of the experiment is to show the formation of amalgam. To prevent the water from acting on the amalgam, there is a layer of chloroform or carbon bisulfid under the aqueous solution. *W. D. B.*

On a Form of the Electric Furnace for the Lecture Table and the Laboratory. *F. W. Küster and F. Dolezalek. Zeit. Elektrochemie,* 3, *329* (*1897*). A description of the way to make a furnace from a block of lime and two carbon electrodes with the help of a saw and a borer. *W. D. B.*

Structure Phenomena

Anomalous Electric Dispersion in Liquids. *P. Drude. Ber. sächs. Akad. Wiss.* 23, *316* ; *Wied. Ann.* 58, *17* (*1896*). Illustrated description of a simple apparatus for determining the absorption of electric waves in liquids, and their refraction and dispersion on passing from air into the liquid. The field used alternated 150 million or 400 million times per second according to the apparatus used ; the length of the electric wave in air was 74 cm.

The most striking result of the measurements is the discovery that the electric waves are extinguished by glycerol as quickly as by a five percent solution of cupric sulfate ; *i. e.*, that as measured with these rapidly alternating electric fields these two substances conduct equally well, although for the comparatively slowly changing current from an induction coil (Kohlrausch's method) their resistances stand in the ratio of 6000 : 1.

Further investigation shows that this remarkable rise in the apparent conductivity may be noticed in the case of other substances with high molecular weights, *e.g.*, amyl alcohol, acetic acid, anilin, whose dielectric constants vary much from the square of the optical refraction exponent. In all such cases there was observed in addition, abnormal dispersion and absorption *i. e.* the electric refraction exponent *decreased*, and the absorption *increased* with increase in the number of alternations of the field.

The dielectric constant of *water*, on the other hand, as determined by the new method, is within one percent of that found by methods involving the use of currents from the ordinary induction coil. *W. L. M.*

Bolometric Investigation of the Absorption Spectra of Several Fluorescent Substances, etc. *B. Donath. Wied. Ann.* **58**, *609 (1896)*. The measurements were very carefully carried out with specially constructed apparatus. The spectrometer was provided with a quartz prism and with a system of mirrors in place of lenses; a circular form of Wheatstone's bridge was designed in order to avoid thermal currents; and the whole apparatus was so arranged that all adjustments could be made from the observer's position at the reading telescope of the galvanometer.

Fourteen substances were examined between the limits $\lambda = 0.6\mu$ and $\lambda = 2.7\mu$; with the following results:—

1. No absorption bands were observed in the case of the fluorescent substances uranin, eosin, fluorescein, oesculin and chlorophyll; the bearing of this result on v. Lommel's theory of fluorescence is discussed.

2. The absorption curve of a solution of alum in water, saturated at 20°*C*, is identical with that of pure water.

3. The absorption curve of the following substances proved to be *identical*, in spite of their very different chemical constitutions, viz:—turpentine, the oils of juniper, of rosemary, of lavender and of sassafras, olive oil, petroleum.

4. Measurements with solutions of chlorophyll within the limits of the visible spectrum, showed evidence of a strong absorption between the green and the red, a region where with the spectrometer no trace of any absorption can be noticed. No satisfactory explanation of this remarkable result is offered. *W. L. M.*

Spectrometric Experiments with Stereo-Isomeric Bodies. *J. W. Brühl. Zeit. phys. Chem.* **21**, *385* (*1896*); abstracted in Ber. Chem. Ges. Berlin **29**, 2902 (1896). Measurements of the molecular refraction and dispersion of ten pairs of stereo-isomeric compounds. All measurements were made on solutions; and though the optical properties were found to vary with the nature of the solvent, they remained the same for different concentrations in the same solvent.

The substances studied may be divided into two classes: *a.* halogen derivatives of the unsaturated hydrocarbons, oximes, hydrazons, in which the optical properties of the stereoisomers are identical; *b.* unsaturated acids, their ethers, diazobenzene cyanids, where without exception the more stable, higher melting and less soluble isomer has the greater refractive and dispersive power.

For twelve of the compounds (those containing no nitrogen), values calculated from the chemical constitution are compared with those obtained. In most cases the observed values are higher than the calculated, as is usual with substances containing several optically active groups directly connected. *W. L. M.*

On Ozone and Phosphorescence Phenomena. *M. Otto. Comptes rendus*, **123**, *1005* (*1896*). When ozone and pure water are shaken together in a flask there is no visible action. If the water contain almost any organic substance, a distinct phosphorescence is perceptible. This is an excellent lecture experiment. *W. D. B.*

Action of X-rays on Gaseous Dielectrics. *L. Benoist. Comptes rendus*, **123**, *1265* (*1896*). The author believes that the action of the X-rays in discharging electrified substances is due to convection rather than to dissociation. From his own experiments and those of Perrin he deduces the following theorems: «The rate of discharge by X-rays of a given electrified body under given conditions varies proportionally to the square root of the density of the gas into which it is plunged, whether it is the same gas under different pressures or different gases under the same pressure». «The quantities of electricity set free by the action of the X-rays must be proportional to the absolute temperature for the same gaseous dielectric».

W. D. B.

The Spectrum of Argon. *J. Trowbridge and T. W. Richards. Phil. Mag.* [*5*] **43**, *77* (*1897*). Reviewed in this Journal **1**, 395; from Am. Jour. Sci. [4] **3**, 15 (1897).

The Multiple Spectra of Gases. *J. Trowbridge and T. W. Richards. Am. Jour. Sci.* [*4*] **3**, *117*; *Phil. Mag.* [*5*] **43**, *135* (*1897*). The experiments begun with argon (see preceding note) are continued with other elements. With a continuous discharge, from the Planté battery of 10000 volts, nitrogen gives the usual channelled spectrum, under varying pressure. With an air gap in the circuit, the red bands almost or quite disappear, the glow becomes more violet, and a pure blue fills the capillary. When the condenser was introduced, the color became bluish green, and the channelled spectrum gave place to well known bright lines,—the conditions being similar to those yielding the blue spectrum with argon. When the condenser oscillations are damped by suitable resistance or self induction, a channelled spectrum reappears.

With hydrogen, the oscillatory spectrum is marked by a predominance of the four familiar lines, while the non-oscillatory spectrum can be resolved into a multitude of sharp lines. The spectrum of each of the halogens is changed by the condenser; but oscillations produced no considerable effect on helium. *R. B. W.*

On the Spectra of Heavy and Light Helium. *J. S. Ames and W. J. Humphreys. Astrophys. Jour.* **5**, *97* (*1897*). By both eye and photographic measurements of spectra obtained with a concave grating, six meters wide, having 15000 lines to the inch and a radius of curvature of twelve feet, the authors find no differences among the spectra of various specimens of heavy, light and ordinary helium furnished by Ramsay. This result does not support the conclusion of Crookes, Lockyer, and Runge and Paschen that helium is a mixture of two gases; the authors suggest that the difference between heavy and light helium may be due to an impurity, «which, although occurring in varying amounts, may still give rise to a strong spectrum». *J. E. T.*

On the Effect of Light on Displacement of Bromine and Iodine from Organic Bromides and Iodides. *J. H. Kastle and W.*

A. Beatty. Am. Chem. Jour. **19**, *139* (*1897*). It was found that, in presence of sunlight, moist chlorin will set bromid and iodin free from many organic compounds. In some cases it was shown that the same reaction takes place in the dark within a measurable period of time if the temperature be raised to 100°. *W. D. B.*

Color Reactions of Nitric and Chloric Acids with Certain Aromatic Bodies. *E. C. Woodruff. Jour. Am. Chem. Soc.* **19**, *156* (*1897*). The author added one drop of a nitrate, chlorate, bromate, iodate, bromid or iodid solution to a solution of two grams of an aromatic substance in 100 cc of strong sulfuric acid and then neutralized with caustic alkali, noting the color before and after neutralizing. Among the aromatic substances taken were five phenols, three cresols, two oxyacids, nine amins, alizarin and α-naphthol. With the anilins and toluidins curious fleeting, unexplained changes of color were noticed on diluting with water. *W. D. B.*

The Viscosity of Mercury Vapor. *A. A. Noyes and H. M. Goodwin. Zeit. phys. Chem.* **21**, *671* (*1896*). Reprinted from the Physical Review; reviewed in this Journal **1**, 253.

On an Electrocapillary Experiment. *A. Chassy. Jour. de Phys.* (*3*) **6**, *14* (*1897*). A glass tube is plunged below the surface of mercury in a beaker and the beaker is then filled with dilute acid. If the solution is electrolyzed with the mercury as the anode, the liquid filters into the glass tube. The rate of filtration is a function of the current. *W. D. B.*

On the Influence of the Temperature on the Surface Tension of Water and Other Liquids. *V. Monti. Nuovo Cimento,* (*4*) **5**, *5* (*1897*). Surface tension measurements for water, acetone, anilin, carbon bisulfid, propyl alcohol and ethyl acetate over ranges of temperatures not exceeding twenty degrees. The surface tension increases with rising temperature and seems to be approximately a linear function of the temperature. The different series are not compared so that it is difficult to say how much, if anything, the author has proved. *W. D. B.*

The Dielectric Constant of Liquid Oxygen. *Fleming and Dewar. Proc. Roy. Soc.* **60**, *358* (*1896*). A small condenser composed of thin sheets of aluminum separated by fragments of crown glass, and plunged beneath the surface of the liquid, was charged to 100 volts and discharged into a much larger condenser. This process was repeated ten times and then the larger condenser discharged through a standardized ballistic galvanometer.

As a result of their measurements the authors found $K = 1.491$ as the dielectric constant of liquid oxygen referred to that of the overlying gaseous oxygen at $-182°C$ as unity; or $K = 1.493$ referred to a vacuum. The result of this direct determination comes remarkably close to 1.495 the (theoretical value) of the dielectric constant, as calculated from the refractive index and magnetic permeability of liquid oxygen by Maxwell's law [product of dielectric constant and magnetic permeability equals square of refractive index for waves of infinite wave length].

In a note the authors point out that the magnetic susceptibility of liquid oxygen, Proc. Roy, Soc. **60**, 283 (1896), is nearly twice as great as that of gaseous oxygen for equal masses. The inference is that the magnetic susceptibility is not merely a property of the molecule *per se*, but is a function of the state of aggregation.

W. L. M.

An Experimental Test of the Clasius-Mossotti Formula. *R. Millikan. Wied. Ann.* **60**, *376* (*1897*). The formula for perfectly conducting spheres in a perfect insulator is $K = K' \frac{1+2x}{1-x}$ where K is the dielectric constant of the compound medium, K' that of the insulator and x the fraction of the total volume occupied by the conducting spheres. The dielectric used was an emulsion of water (conducting spheres) in a mixture of C_6H_6 and $CHCl_3$. The measurements were made by Nernst's method and the results obtained for the emulsion agreed satisfactorily with the values calculated from the formula by putting in the known values of K' and x. *E. B.*

Dielectric Constants at Low Temperatures. *R. Abegg. Wied. Ann.* **60**, *54* (*1897*). Measurements at low temperatures by Nernst's method for Specific Inductive Capacity. The freezing mixture used was a mixture of ether and solid CO_2. It was contained in a vacuum beaker of Dewar's form and the test tube containing the liquid to be tested was sunk in the mixture. The liquids used were: Toluol, ether, amyl alcohol, acetone, ethyl alcohol and a mixture of 10 volumes ethyl alcohol with 1 volume water. The temperature coefficient of the dielectric constant, *D*, is in all cases negative and $\partial D/\partial T$ is greater the greater *D* itself is; so that those substances, such as water, which present exceptions to Maxwell's rule regarding the index of refraction, are not to be expected to follow the rule any better at low temperatures. The measurements on the mixture were undertaken to find out whether *D* could be calculated by the ordinary mixture rule. This was found to be the case and, calculating back from the values of *D* for the mixture and for ethyl alcohol separately at low temperatures, the value for water was found to be $D = 137$ at $-80°$. The range of temperature covered by the experiments was from $+19°$ to $-87°$. *E. B.*

On the Temperature-coefficient of the Dielectric Constant. *F. Hasenoehrl. Wien. Akad. Ber.* **105**, *460* (*1896*). Measurements by Gordon's method, Wien. Akad. Ber. **99**, 480 (1890), of the dielectric coefficients of benzene, almond oil, vaseline and paraffin at six different temperatures. Contrary to the experience of Ratz, Zeit. phys. Chem. **19**, 94 (1896), the author finds that the Mosotti-Clausius constant $\frac{K+2}{K-1}d$ (*K* dielelectric constant, *d* density) is practically independent of the temperature, the greatest variation being 0.7 percent for a temperature interval of $30° - 40°$C. The measurements of the dielectric constant of paraffin given in this paper, furnish the first application of the theory to the case of solids.

W. L. M.

The Crystalline Form of Optically Active Substances. *P. Walden. Ber. Chem. Ges. Berlin.* **30**, *98* (*1897*). In contradiction of the statement of Traube, see this Journal, **1**, 333 (1897), that «in no case in which a complete crystallographic examination has been made has an exception to Pasteur's law of hemihedral forms been discovered» the author quotes the cases of certain derivatives of camphor, where a critical examination of geometric form, etch lines and pyroelectric behavior has given no evidence of hemihedral structure. He points out the remarkable dependence of the crystalline form on the temperature of crystallization and on the nature of the solvent, and insists on the importance of a thoroughgoing experimental study of the whole subject. *W. L. M.*

MASS LAW STUDIES, II

BY S. F. TAYLOR

When to two practically non-miscible liquids a third is added which is consolute with the other two, there are present two liquid phases and a vapor phase. All three components are present in all three phases and with increasing concentration of the third liquid there is a change in the composition of each of the three phases. The changes in the vapor phase do not form part of the present discussion and will not be referred to again. The changes in the compositions of the two liquid phases are such that these two phases become more nearly alike with increased addition of the third liquid; eventually become identical and disappear, leaving the trivariant system, solution and vapor. While there are measurements[1] on record giving the different relative proportions in which two non-miscible liquids and a consolute liquid may be combined in order to form a saturated solution at a given temperature, there are almost no observations showing what solutions form stable pairs. In other words we have very little knowledge of the composition of coexistent liquid phases. At the request of Professor Bancroft, I have analyzed six mixtures of benzene, water and alcohol. Before describing the methods and the results it will be well to point out the general form of the relations for this system.[2] Let x_1 refer to the water in the upper liquid phase, x_2 to the water in the lower liquid phase, y_1, y_2 and z_1, z_2 to benzene and alcohol respectively. It is entirely immaterial what units are selected. In any case x/z will represent the amount of water with reference to alcohol and x/V the amount of water with reference to the volume of the solution. If z and V are kept constant and made

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[1] Pfeiffer. Zeit. phys. Chem. **9**, 444 (1892); Bancroft. Phys. Rev. **3**, 21 (1895).

[2] I am indebted to Professor Bancroft for the theoretical treatment.

equal to unity x/z becomes x and denotes the amount of water in unit quantity of alcohol while x/V becomes x also but denotes the amount of water in unit volume of the solution. Since care will be taken to specify what variable is kept constant in any particular case, there should be no room for confusion. Applying Wenzel's statement of the Mass Law[1] that the strength of the chemical action is proportional to the concentration of the acting substance, we shall have $x_1^{n_1}y_1/z_1^{n_1+1} = C_{n_1}$ for the upper liquid phase and $x_2^{n_2}y_2/z_2^{n_2+1} = C_{n_2}$ for the lower liquid phase where n_1 and n_2 are constants but not necessarily integers. In the particular case of water, benzene and alcohol, it has been found experimentally that $n_1 = n_2$ whence it follows that $C_{n_1} = C_{n_2}$ because we can pass continuously from one liquid phase to the other. Dropping the superfluous subscripts we may write :

$$\frac{x_1^n y_1}{z^{n+1}} = \frac{x_2^n y_2}{z^{n+1}} = C \qquad \text{I}$$

By a similar application of the Mass Law we see that the concentrations in the two coexisting liquid phases will be described, when $z_1 = z_2 =$ unity, by the equations :

$$x_1^m x_2 = C_1 \quad (1) \text{ and } \quad y_1^m y_2 = C_2 \qquad (2)$$

In these equations x_1, x_2, y_1 and y_2, denote the concentrations of water and benzene respectively, in the two phases, referred to constant unit quantity of alcohol while m, like n, is a constant but not necessarily an integer. From equations I and (1) there follows a series of relations. If we express the water and alcohol with reference to a constant unit quantity of benzene we may write :

$$x_1^m x_2 = C_3 \quad (3) \text{ and } \quad z_1^m z_2 = C_4 \qquad (4)$$

If such quantities of the two phases are considered that the amount of water in each is always constant and equal to unity we shall have

$$y_1^m y_2 = C_5 \quad (5) \text{ and } \quad z_1^m z_2 = C_6 \qquad (6)$$

If all three components vary while the volume remains constant we have :

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[1] Ostwald. Lehrbuch 2, II, 40.

$$\left(\frac{x_1y_1}{z_1^2}\right)^m\left(\frac{x_2y'_2}{z_2^2}\right) = C' \qquad \text{II}$$

The relations among the constants are shown by the following equations:

$$C_1 = 1/C_6 = C_3/C_4 = C_2C_3 \qquad (7)$$

$$C_2 = 1/C_4 = C_5/C_6 = C_1C_5 \qquad (8)$$

$$C' = C_1C_2 \qquad (9)$$

Since $x_1 = x_2$, $y_1 = y_2$ and $z_1 = z_2$ when the two liquid phases become identical, we also have the relation:

$$\log C = \frac{n \log C_1 + \log C_2}{m + 1} \qquad (10)$$

If we use capital letters to denote the amounts of water, benzene and alcohol in a given volume of the solution at the moment when the two phases become identical we may write:

$$C = C'\frac{Z^{2m-n+1}}{X^{m-n+1}Y^m} \qquad (11)$$

It should be kept in mind that if equations I and (1) hold, the others necessarily follow, being merely algebraical transformations. Equation I has already been shown to describe the variations in composition of each of the liquid phases in the divariant ternary system, two solution phases and vapor, so that the primary object of this paper is to test the validity of equation (1) and to determine the value of the exponential factor m.

Since mixtures, of water, benzene and alcohol can not be analyzed with any comfort gravimetrically, it was thought advisable to make use of an optical method. The temperature at which the measurements were to be made was 25° since I had already made a series of determinations for the single phases at that temperature. Solutions were made up containing five cubic centimeters of alcohol and varying but accurately known amounts of benzene and water. These latter quantities were so chosen that the solutions were exactly saturated at 25°. These solutions were warmed to 26° to prevent any danger of precipitation and the index of refraction for that temperature was determined by means of a Pulfrich's refractometer. Laying off the amounts of benzene or of water in the solutions along one axis and the indices of refraction along the other, it was possible to plot the results in a curve and the composition of any solution saturated at 25° could then be determined by interpolation on the curve if its index of refraction for 26° were known. It was found that the range of concentrations covered by my previously published experiments[1] was altogether too limited for the present purpose. On extending it I found that the formula, $1.85 \log x + \log y = 0.812$, continued to describe the phenomena even when I had fifty cubic centimeters of benzene in five cubic centimeters of alcohol. In table I are given the data from which I constructed my curve. The first three columns give the amounts of the three components in the solutions and the fourth column the indices of refraction with reference to the sodium flame.

TABLE I

C_6H_6	H_2O	C_2H_5OH	Index
50.	0.33	5.00	1.48383
40.	0.37	5.00	1.48151
30.	0.44	5.00	1.47597
20.	0.55	5.00	1.46627
10.	0.79	5.00	1.44226
5.0	1.15	5.00	1.41758
4.0	1.30	5.00	1.41035
3.0	1.52	5.00	1.40066
2.0	1.90	5.00	1.38972
1.8	2.00	5.00	1.38650
1.0	2.75	5.00	1.37551
0.85	3.00	5.00	1.37048
0.50	4.00	5.00	1.36432
0.33	5.00	5.00	1.36072

The actual experiments were made by putting different amounts of the three components into stoppered test tubes, letting the system stand at 25° until the two solution phases were perfectly clear, pipetting off portions of each layer, warming them to 26° and determining the indices of refraction. A few preliminary experiments served to show in what proportions the three components should be taken in order to get enough of each of the layers to make it possi-

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[1] Jour. Phys. Chem. 1, 301 (1897).

ble to pipette them off with comfort and at the same time to ensure a sufficient range of concentrations. In Table II are given the experimental data as found from the curve. The Roman numerals serve to identify the six systems. In the second column are the cubic centimeters of benzene in an amount of the upper layer such that it contains five cubic centimeters of alcohol synthetically. In the third column are the values for water also expressed in cubic centimeters and referred to five cubic centimeters of alcohol as the constant unit. In the fourth and fifth columns are the corresponding values of benzene and water for the lower layer. In the sixth column are the values for the constant obtained from the equation

$$1.55 \log y_1 + \log y_2 = \text{const}$$

by taking for y_1, the values of benzene given in the second column of the table and for y_2 the values of benzene given in the fourth column of the table. The values for solution VI were determined by extrapolation and are therefore not as accurate as those for the other solutions.

TABLE II

	Upper layer		Lower layer		
	C_6H_6	H_2O	C_6H_6	H_2O	Const.
I	8.5	0.86	4.8	1.18	2.122
II	10.4	0.77	3.5	1.40	2.120
III	16.0	0.61	1.8	2.00	2.121
IV	24.0	0.49	0.95	2.83	2.117
V	34.5	0.40	0.55	3.80	2.124
VI	51.0	0.33	0.3	5.27	2.124

It will be seen that there is only a very slight variation in the constant; in fact the change is so slight that there is danger of conveying a false idea with regard to the accuracy of the experiments. Fortunately, the data to be given in table VI will offset this to a certain extent.

The qualitative relations shown in Table II are very surprising. I had supposed that in the upper layer the ratio of benzene to water would always exceed unity and that in the lower layer this would be reversed. On this assumption the two phases would become identical when the ratio of benzene to water was unity. If this were true when the quantities of benzene and water were expressed in one set of units, it would no longer be true of another set of units. It would be rather an interesting problem—though not coming within the scope of this paper—to consider whether for some set of units one could establish the proposition that the ratio of one of the non-miscible liquids to the other is necessarily greater than unity in one liquid phase and less than unity in the other and, if this were established, to determine what those units should be. If one expresses the results in cubic centimeters, the relation does not hold for water and benzene in the presence of ethyl alcohol. In solutions I and II the ratio of benzene to water is greater than unity in both solution phases. If the concentration is expressed in reacting weights instead of in cubic centimeters, there is always more water than benzene in the lower layer and more benzene than water in the upper layer—at least so far as these six sets of measurements go. If it should be shown that for some set of units, the ratio of the two non-miscible liquids becomes unity at the point where two liquid phases cease to be possible, we could write equation (11) in the form

$$C = C'\frac{Z^s}{X^s} = C'\frac{Z^s}{Y^s} \qquad (12)$$

by making $s = 2m - n + 1$, since $X = Y$ by definition.

The constant in the sixth column of Table I is not any of the constants in equations 1–12 but we can easily pass from it to them. If the concentrations of benzene and water had been expressed with reference to one cubic centimeter of alcohol, the constant in the table would have been equal to log C_1. By subtracting 2.55 log 5 we shall have log C_2. In table III I have tabulated the values of the logarithms of the six constants in equations 1–6 as obtained from my experiments. the unit being the cubic centimeter and setting $m = 1.55$.

The actual volume concentrations of the solutions can not be determined from my experiments because we do not know how much expansion or contraction there is when water, benzene and alcohol are mixed in varying proportions; but this is not of the slightest importance so far as the quantitative relations which interest us are

TABLE III

	$\log C_1$	$\log C_2$	$\log C_3$	$\log C_4$	$\log C_5$	$\log C_6$
I	0.189—2	0.340	0.849—3	0.660—1	2.151	1.811
II	0.191—2	0.338	0.853—3	0.662—1	2.147	1.809
III	0.190—2	0.339	0.851—3	0.661—1	2.149	1.810
IV	0.194—2	0.335	0.859—3	0.665—1	2.141	1.806
V	0.187—2	0.342	0.845—3	0.658—1	2.155	1.813
VI	0.187—2	0.342	0.845—3	0.658—1	2.155	1.813
	0.190—2	0.339	0.851—3	0.661—1	2.149	1.810

concerned. Professor Bancroft[1] has shown that the term for the volume disappears when considering one phase and the same proof applies in the same way to two coexistent phases. Let V_1 be the volume of the upper liquid phase and V_2 the volume of the lower liquid phase taken for analysis. Dividing the amount of each of the components, expressed in any units whatsoever, by the volume of the solution gives the concentration per unit volume. Substituting these values in equation II we get:

$$\left(\frac{\frac{x_1}{V_1}\,\frac{y_1}{V_1}}{\left(\frac{z_1}{V_1}\right)^2}\right)^m \left(\frac{\frac{x_2}{V_2}\,\frac{y_2}{V_2}}{\left(\frac{z_2}{V_2}\right)^2}\right) = C'$$

Since V_1 and V_2 cancel out, we come back to equation II, thus showing that the actual volume occupied by any given quantity of the solution does not appear in the equations which describe these phenomena. A contraction or expansion on mixing will increase or decrease the volume concentration of each of the components; but it changes them all in the same ratio and therefore does not change the relative concentrations. If the determinations of water, benzene and alcohol had been expressed in grams, it would be natural to show the way in which the three components vary simultaneously by giving the concentration of each component in one hundred grams of the solution. Since my measurements are given in cubic centimeters I shall tabulate the data, giving the values in cubic

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[1] Phys. Rev **3**, 116 (1895).

centimeters of each component in ten cubic centimeters of the solution synthetically, in other words the volume concentrations in cubic centimeters per ten cubic centimeters if there were neither expansion nor contraction on mixing. This is done in Table IV, there being added in the eighth column the values of log C' as calculated from equation II.

Table IV

	Upper layer			Lower layer			
	C_6H_6	H_2O	C_2H_5OH	C_6H_6	H_2O	C_2H_5OH	log C'
I	5.92	0.60	3.48	4.37	1.07	4.56	0.529—2
II	6.43	0.48	3.09	3.54	1.41	5.05	0.528—2
III	7.40	0.29	2.31	2.04	2.27	5.69	0.529—2
IV	8.13	0.17	1.70	1.08	3.22	5.70	0.527—2
V	8.65	0.10	1.25	0.59	4.06	5.35	0.530—2
VI	9.05	0.06	0.89	0.28	4.99	4.73	0.531—2

The changes in the constant, log C', are necessarily of the same order as in the first two tables and merely show that there have been no errors in the algebraical transformations. Of more interest are the qualitative changes in the concentration of alcohol in the lower layer. Instead of increasing continuously it passes through a maximum and decreases. This was entirely unexpected and the possibility of such a thing has never even been suggested. This apparently anomalous behavior has, of course, nothing to do with the choice of units. It would remain just the same if the concentrations were expressed in reacting weights per liter.

If we know the total amounts of the water, benzene and alcohol in the two liquid phases, and the concentrations of those two phases, it is possible to calculate the amount of each phase which will be formed from the original mixture and thus check the accuracy of the results. Since it would be very difficult to separate the two phases completely and weigh each without loss, the next way would be to measure the volumes of the solutions formed. This would be thoroughly unsatisfactory except in the ideal case in which neither contraction nor expansion occurs. What we can do is to turn the problem round and see whether quantities of the two phases could be found such that the total amounts of water, benzene and alcohol in the two phases should equal the initial masses or volumes of the three components which had been taken to form the system under consideration. This has been done and the results are given in Table VI. Since absolute agreement was not to be expected it became a question whether to divide the variations up among the three components thus minimizing the apparent error or to solve for the amounts of the two phases necessary to make the calculated quantities of two of the components equal the experimental values, concentrating the error upon the third component. I have adopted the latter course with the first four solutions and the former with the last two. In Table V are given the number of cubic centimeters of each phase, synthetically, which are assumed in calculating the values in Table VI. Of course the sum of the two phases would add up twenty cubic centimeters if there were no experimental error. Equally of course, that ideal condition is not realized in any single case. In the second, third and fourth columns of Table VI are the values for benzene, water and alcohol in cubic centimeters calculated from the experimental concentrations of the phases and the data in Table V. In the fifth, sixth and seventh columns are the quantities of benzene, water and alcohol in cubic centimeters which were taken to form the solutions I–VI.

TABLE V

I	13.32	6.73	IV	10.3	9.4
II	12.7	7.5	V	10.2	9.8
III	10.53	9.42	VI	10.2	9.7

TABLE VI

	Calculated			Found		
	C_6H_6	H_2O	C_2H_5OH	C_6H_6	H_2O	C_2H_5OH
I	10.82	1.63	7.70	10.83	1.65	7.70
II	10.81	1.67	7.70	10.80	1.73	7.70
III	9.70	2.45	7.79	9.70	2.50	7.80
IV	9.39	3.20	7.10	9.40	3.50	7.10
V	9.40	4.08	6.50	9.40	4.30	6.30
VI	9.50	4.91	5.50	9.45	4.90	5.07

The relations given in equations 1–6 describe the distribution of one component between two phases when one of the other components is kept constant and equal to unity in both phases. By substituting from equation I in equations 1–6 we can get the expression for the simultaneous concentrations of one component in one phase, and another in the other phase, the concentration of the remaining component being kept constant and equal to unity in both phases. These new equations will all hold absolutely provided equations I and (1) are absolutely accurate.

When $z_1 = z_2 =$ unity we have:

$$x_1^{mn}/y_2 = C_1^n/C = C^m/C_2 \qquad (1a)$$

$$y_1^m/x_2^n = C_2/C = C^m/C_1^n \qquad (2a)$$

When $y_1 = y_2 =$ unity we have:

$$x_1^{mn} \quad z_2^{n+1} = C_3^n/C = C_4^{n+1}C^m \qquad (3a)$$

$$z_1^{mn+m}x_2^n = C_4^{n+1}C = C_3^n/C^m \qquad (4a)$$

When $x_1 = x_2 =$ unity we have:

$$y_1^m \quad z_2^{n+1} = C_5/C = C_6^{n+1}C^m \qquad (5a)$$

$$z_1^{mn+m}y_2 = C_6^{n+1}C = C_5/C^m \qquad (6a)$$

In addition there are a series of relations for the distribution of one component between the two phases when one of the other components is kept constant in one phase and the remaining one in the other phase. They may be deduced from the preceding six equations by substituting for the conditions there imposed the conditions that what are now variables in those equations shall be constant and equal to unity. Doing this we get the following results:

When $x_1 = y_2 =$ unity we have:

$$z_2/z_1^{mn} = C_1^n/C \qquad (1aa)$$

When $y_1 = x_2 =$ unity we have:

$$z_2^n/z_1^m = C_2/C \qquad (2aa)$$

When $x_1 = z_2 =$ unity we have:

$$y_1^{mn}y_2^{n+1} = C/C_3^n \qquad (3aa)$$

When $x_2 = z_1 =$ unity we have:

$$y_1^{mn+m}y_2^n = 1/C_4^{n+1}C \qquad (4aa)$$

When $y_1 = z_2 =$ unity we have:

$$y_1^m x_2^{n+1} = C/C_5 \qquad (5aa)$$

When $z_1 = y_2 =$ unity we have:

$$x_1^{mn+m} x_2 = 1/C_6^{n+1} C \qquad (6aa)$$

Of this last batch of equations only the one marked (*2aa*) is of any importance. Letting $n/m = p$ and condensing the constants in the equation into a single one the relation may be written in the form:

$$z_2^p/z_1 = \textit{constant} \qquad \text{III.}$$

Here z_2 is the amount of alcohol in a constant quantity of water and z_1 the amount of alcohol in a constant quantity of benzene. This is the form in which Nernst should have deduced his Distribution Theorem.[1] The actual form differs only slightly from this but the difference is fundamental. Nernst writes the equation as follows:

$$c_2^n/c_1 = \textit{constant} \qquad \text{IV}$$

where c_2 is the concentration of alcohol in the lower or aqueous layer, expressed in reacting weights per liter of the solution, c_1 is the concentration of alcohol in the upper or benzene layer expressed in the same units, while n is a constant and an integer, equal to one when the reacting weight of alcohol is the same in the two solvents. Equation IV is deduced on the express condition that the two non-miscible liquids do not become more soluble in each other with increasing addition of the consolute liquid—a condition which is never fulfilled theoretically. Equation III is free from this restriction and contains only the assumption—made also in deducing equation IV—that the equilibrium between the phases is described by the Mass Law. Equation III is therefore applicable to all concentrations, equation IV only to unrealizable ones. For very dilute solutions and for cases where the exponential factor p does not differ much from unity, the two equations III and IV will give practically the same results because in very dilute solutions the mass and the volume concentrations are proportional, while the slight differences between the experimental values and those calculated from equation IV can be attributed to association or dissociation. With increasing

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[1] Zeit. phys. Chem. 8, 110 (1891).

concentration of alcohol a comparison between the equations becomes superfluous because one describes the facts and the other does not.

From the data which we already have it is possible to calculate all the constants in equation III. Since $n = 1.85$ and $m = 1.55$ $n/m = 1.19$ because the accuracy with which n and m are known does not justify another decimal place in the quotient. The constant in the equation is equal to the mth root of C_2/C. Since log $C = 0.820-2$ and log $C_2 = 0.339$ the logarithm of the constant will be 0.98. This refers to the concentration of alcohol in cubic centimeters by synthesis in one cubic centimeter of water for one phase and in one cubic centimeter of benzene for the other. If we wish to express the concentrations with respect to five cubic centimeters of water and benzene respectively we must add 0.19 log 5 to this value which gives us 1.113 for the logarithm of the constant and 12.96 for the constant itself. The experimental value is 12.91 and this discrepancy of less than one-half of one percent would be wiped out if the value of n/m had been carried out to one more place of decimals. In the second column of Table VII are the concentrations of alcohol expressed in cubic centimeters by synthesis per five cubic centimeters of benzene in the upper layer;[1] in the third column are the concentrations of alcohol in the lower phase, expressed in cubic centimeters and referred to five cubic centimeters of water as the unit. In the fourth column are the values of the constant as calculated from these data by the formula

$$(5z_2)^{1.19}/(5z_1) = const$$

while in the fifth column is the predicted value of this constant.

TABLE VII

	$5z_1$	$5z_2$	const	calc.
I	2.94	21.2	12.91	12.96
II	2.41	17.9	12.88	12.96
III	1.56	12.5	12.94	12.96
IV	1.04	8.77	12.74	12.96
V	0.73	6.59	12.91	12.96
VI	0.49	4.72	12.91	12.96

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[1] Deduced from Table II.

In this paper there is given a complete discussion of the equilibrium between two liquid phases at constant temperature for systems made up of two non-miscible liquids and a third consolute with the other two, when the whole isotherm can be presented by a single equation. The relations deduced have been tested by means of experiments upon the system, benzene, water and ethyl alcohol. It is also shown that one must use mass concentrations in expressing the distribution of a substance between two liquid phases.

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SOLUBILITY AND FREEZING-POINT

BY D. MC INTOSH

If we add to a binary solution, made up of the components A and B, a third component C which is non-miscible with A, the partial pressure of this latter substance will be increased. A striking instance of this was noted by Bussy and Buignet[1] with the cyanids and hydrocyanic acid. In this case the twe substances which are to be treated as non-miscible have a common ion. Roloff[2] has shown that addition of potassium chlorid to an aqueous solution of acetic acid increases the partial pressure of the acid; but he has apparently dropped the subject as not worth further study. Very recently, Freyer[3] has shown that if sugar be added to aqueous alcohol the boiling point of the solution is lowered and not raised. But one explanation of this phenomena seems possible. The addition of sugar to the solution must decrease the partial pressure of the water vapor and the observed increase in the total pressure of the system must be due to the precipitation of alcohol by sugar. Since sugar is not soluble in alcohol, it could have been predicted that the partial pressure of the alcohol vapor would increase with addition of sugar to the solution though there are as yet no data on which to base any quantitative predictions. If the substance A can exist as a solid phase at the temperature of the experiment, the addition of C will make the solution more nearly saturated with respect to A. If the concentration of A be sufficiently high this substance will be precipitated by C. When alcohol is added in sufficient quantity to almost any salt solution, there is precipitation of salt. If we adopt Ostwald's definition that that which separates is solvent, we should

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[1] Comptes rendus, 58, 841 (1864).

[2] Zeit. phys. Chem. 11, 23 (1893).

[3] Zeit. angew. Chem. 654 (1896).

call this a case of a rise of freezing point. This is not really the case. It has already been shown that the curve for the system, salt, solution and vapor, is a solubility curve and not a fusion curve so that when we add alcohol to a saturated salt solution we are precipitating one solute by another. It is a case of diminished solubility and not one in which we may speak of a rise of freezing point, though qualitatively the two phenomena are the same.

There is no difficulty in finding an instance that is not open to the above objection. If we add alcohol to benzene we lower the freezing point of the latter. On adding water in insufficient quantities to produce a second liquid phase we should expect to find the freezing point of the benzene raised. We should thus have the unusual phenomenon of a solution freezing at higher and higher temperatures the more concentrated it becomes, in spite of the fact that it is pure solvent that separates. I have been able to find only one recorded instance of this and that a very unsatisfactory one. Roloff[1] determined the freezing points of mixtures of benzene, acetic acid and water, water and benzene being the two non-miscible substances. He starts with benzene and water and adds acetic acid in varying amounts. He finds that, for a given ratio of benzene to acetic acid, the benzene freezes at higher and higher temperatures depending on the amount of water present. Since there are two liquid layers present he has no difficulty in explaining this. Some of the acetic acid passes into the aqueous phase and the real concentration in the benzene phase is thus less than it would be if no water were present. He adds: «It is especially to be noticed that, as far as the course of the curves is concerned, it makes no difference whether water and benzene occur in two coexisting liquid phases or whether they form a homogeneous solution (on addition of enough acetic acid).» From this one is justified in concluding that Roloff might have observed a rise of freezing point if he had added acetic acid to benzene and then water instead of proceeding in the opposite order. While he has thus stated the fact that presence of water raises the freezing point of solutions of acetic acid in benzene, he does not state which, if any, of his published measurements refer to

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[1] Zeit. phys. Chem. **17**, 353 (1895).

systems with only one liquid phase. He offers no explanation of the phenomenon and evidently regards it as of minor importance.

Matters being in this state I have, at the suggestion of Professor Bancroft, made some experiments in order to bring out more clearly the relations between solubility and freezing point in ternary mixtures.

When we have two non-miscible substances A and C and a third substance B with which the other two are miscible we can distinguish two cases. I. The component A can exist as solid phase under the conditions of the experiment. Under these circumstances addition of C to the liquid phase containing A and B will raise the temperature at which A can exist as solid phase. That is the case which we have been discussing.

II. The component B can exist as solid phase under the conditions of the experiment. Under these circumstances addition of B to the liquid phase containing A and B will lower the temperature at which B can exist as solid phase and this lowering will be more than it would be if A and C were miscible to some extent. This proposition will be discussed and tested later in the paper.

The first experiments to test Case I were made with benzene, methyl alcohol and water in the hope that methyl alcohol might present some special advantages in the way of solvent power. This proved not to be the case, so I changed to ethyl alcohol as being cheaper and satisfactory in all respects. The benzene used had been previously purified by crystallization, treatment with sodium and fractional distillation. As it had been standing in the bottle nearly three years since that time, I recrystallized it twice. The methyl alcohol was dried over anhydrous copper sulfate and subjected to fractional distillation. The ethyl alcohol was treated first with lime, then with copper sulfate and distilled. The water was the distilled water of the laboratory and the measurements were made with the ordinary Beckmann apparatus. The freezing mixture was made of salt and ice and, since its temperature was often eight degrees below the freezing point of the solutions, it is clear that no great accuracy can be claimed for the measurements. Each freezing point was determined twice and the mean taken. When these values differed by more than *0.05°* another determination was made.

With methyl alcohol and benzene three solutions were taken and water added to these. Each solution contained one hundred grams of benzene but there were *36.03* g methyl alcohol in the first, *56.62* g methyl alcohol in the second and *62.60* g methyl alcohol in the third. The absolute freezing points of these solutions were not determined, only the change on adding water. In all cases great care was taken to be sure that no second liquid phase was formed. In Table I are the data for the system, benzene, methyl alcohol and water. Under the heading «water» are given the grams of water per hundred grams of benzene instead of the actual amount of water added. Under Δ are the changes in the freezing points. In this, as in succeeding tables, the plus sign denotes a rise of temperature and the minus sign a fall.

TABLE I

Solution I 100 g benzene 38.03 g CH$_3$OH		Solution II 100 g benzene 56.62 g CH$_3$OH		Solution III 100 g benzene 62.69 g CH$_3$OH	
Water	Δ_1	Water	Δ_2	Water	Δ_3
0.07	+0.08°	0.40	+0.46°	0.57	+0.51°
0.65	0.54	1.18	0.97	1.25	1.05
1.11	0.90	1.55	1.26	2.96	2.30
1.58	1.23	3.09	2.42	4.63	3.36
2.06	1.59	3.85	2.96		
2.53	1.83	4.73	3.30		

It will be noticed that the freezing point does rise and that we are not dealing with imperceptible variations. In the second and third solution the rise was more than three degrees. It was not part of the original plan of the paper to attempt to express the rise of freezing point mathematically in terms of the amount of water added since the chief object was to establish the purely qualitative fact of a rise of freezing point. Having the data at my hand, however, it seemed a pity not to see whether any relations could be discovered. On plotting the data for the three solutions, using the logarithm of the amount of water added as one coordinate and the logarithm of the rise of temperature as the other, I was surprised to find that all the points lay on a straight line. In other words the data can be expressed by an equation of the form:

$$\frac{g^n}{\Delta} = constant \qquad (1)$$

where g is the number of grams of water per one hundred grams of benzene, while Δ is the rise of temperature. This differs from the van 't Hoff-Raoult formula for the change of the freezing point of a binary solution with the concentration in that n is necessarily unity in the latter formula while for these experiments we have empirically $n = 0.9$. In Table II are given the calculated data for the change of temperature with changing concentration, obtained by means of the formula:

$$0.9 \log g - \log \Delta = 0.076$$

TABLE II

Δ_1 calc	Δ_1 found	Δ_2 calc	Δ_2 found	Δ_3 calc	Δ_3 found
0.09°	0.08°	0.37°	0.46°	0.51°	0.51°
0.57	0.54	0.97	0.97	1.03	1.05
0.92	0.90	1.25	1.26	2.23	2.30
1.27	1.23	2.32	2.42	3.33	3.36
1.64	1.59	2.83	2.96		
1.94	1.83	3.40	3.39		

While the significance of the constants in the formula is not known, the equation seems to represent the facts. It was to be expected that the exponential factor would not change with varying amounts of methyl alcohol; but it is very remarkable that the integration constant remains unaltered. This must be a coincidence and I have not found it to hold true when ethyl alcohol is substituted for methyl alcohol. It is possible that the three curves do not coincide exactly even in this case. A slightly closer agreement between formula and fact could be obtained by using somewhat different integration constants in the three series; but this savors too much of arbitrariness in view of the fact that the differences do not exceed the experimental error.

With benzene, ethyl alcohol and water I wished to make some determinations along the isotherms in order to see how the relative quantities of alcohol and water could vary at constant temperature and still have benzene as solid phase in equilibrium with the solution. To do this it was necessary to know the differences between the freezing points of the various benzene-alcohol mixtures. Since the freezing points were followed for a range of nearly ten degrees it was necessary to reset the thermometer; but it is hoped that no considerable error was thus introduced. The results are given in Table III. Under «alcohol» are grams of alcohol per hundred grams of benzene and under «Δ found» the observed changes in freezing point.

TABLE III

Alcohol	Δ found	Δ calc	Alcohol	Δ found	Δ calc
3.53	—1.67°	—1.75°	44.17	—4.90°	—4.87°
5.21	2.03	2.05	45.17	4.93	4.93
7.16	2.33	2.33	51.10	5.41	5.26
8.51	2.49	2.49	55.28	5.52	5.57
9.41	2.60	2.60	62.10	5.86	5.97
11.67	2.82	2.83	73.92	6.55	6.62
17.60	3.34	3.32	78.39	6.96	6.86
19.12	3.40	3.44	81.23	6.98	7.01
22.37	3.60	3.67	87.45	7.33	7.33
29.72	4.03	4.11	93.32	7.77	7.62
34.21	4.33	4.35	100.10	8.51	7.95
44.17	4.90	4.82	113.07	8.91	8.55
45.17	4.93	4.87	123.52	9.55	9.02

The lowering of the freezing point is surprisingly small. Forty-six grams produce a change of only about five degrees while the depression with ninety-two grams is but a trifle over seven and one-half degrees. The form of the curve is rather curious. When plotted on logarithmic coordinate paper there seems to be a change of curvature when there are fifty grams of alcohol to one hundred grams of benzene. It is not very strongly marked and may be due to experimental error. It does not seem probable that there should be a point of discontinuity here because there is no new solid phase which can separate so far as is now known. The first portion of the curve on the logarithmic paper is surprisingly like a straight line while the second portion varies perceptibly from a straight line only in the last three measurements. It is therefore possible to represent the range of temperatures covered by my measurements by the two empirical formulas:

$$0.4 \log g - \log \Delta = 0.975 - 1$$

$$0.6 \log g - \log \Delta = 0.300$$

The values under «calc» in Table III were obtained from these equations, the first equation giving the results in the third column and the second the results in the sixth column. Whether these equations have any real significance is a question which I am unable to answer. Merely as interpolation formulas they are interesting and may prove useful.

Beckmann[1] has made some determinations with benzene and alcohol but his results do not agree with mine. He finds that *32.45* g alcohol lower the freezing point of benzene five degrees while my measurements show that forty-eight grams are necessary. Curiously enough, if we assume that Beckmann's data were given as grams of alcohol in one hundred grams of solution, his results agree absolutely with mine. In the first column of Table IV is the amount of alcohol as given by Beckmann; in the second the amount of alcohol per hundred grams of benzene if the figures in the first column refer to grams of alcohol per hundred grams of solution; in the third column the observed depressions of the freezing point.

TABLE IV

$Alc._1$	$Alc._2$	Δ
3.483	3.60	−1.705°
5.811	6.17	2.220
8.843	9.71	2.725
14.63	17.14	3.445
22.58	29.18	4.180
32.45	47.97	5.000

While it seems most improbable that any experimental errors could be exactly eliminated by such a correction, it is even more

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[1] Zeit. phys. Chem. **2**, 728 (1888).

improbable that Beckmann should have made such a mistake in giving the concentrations of his solutions. Since presence of water would raise the freezing point, it is quite possible that the discrepancy between the two sets of results may be due to traces of water in my alcohol.[1]

To five different mixtures of benzene and alcohol I added water and determined the rise of freezing point. The data are given in Table V the values for the ethyl alcohol and the water being grams of those substances in one hundred grams of benzene.

TABLE V

I 70.65 g Alcohol

Water	Δ_1 found	Δ_1 calc
0.55	+0.30°	+0.35°
0.99	0.55	0.55
2.33	1.05	1.05
4.15	1.63	1.62
4.82	1.87	1.81
6.92	2.16	2.37
8.30	2.69	2.78

II 72.52 g Alcohol

Water	Δ_2 found	Δ_2 calc
1.74	+0.88°	+0.89°
4.43	1.97	2.07
8.67	3.22	2.97

III 75.47 g Alcohol

Water	Δ_3 found	Δ_3 calc
2.48	+1.71°	+1.70°
4.79	2.77	2.79
5.82	+3.38°	+3.23°
9.70	4.74	4.73
12.38	5.51	5.69
15.33	6.11	6.67

IV 94.66 g Alcohol

Water	Δ_4 found	Δ_4 calc
1.15	+0.41°	+0.95°
3.85	2.20	2.34
6.22	3.60	3.35

V 122.77 g Alcohol

Water	Δ_6 found	Δ_6 calc
7.00	+3.00°	+3.17°
11.18	4.53	4.50
13.38	5.27	5.15
16.09	5.92	5.92
18.97	6.71	6.71

Here again we get a striking confirmation of the theory that addition of a third substance, insoluble in the solvent, raises the freezing point of the latter even when no second liquid phase is formed. In

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[1] Tanatar finds even more of a depression than Beckmann, Zeit. anorg. Chem. **12**, 229 (1896).

solution III the temperature at which solid benzene can exist in equilibrium with the solution has been brought to within less than a degree of the freezing point of pure benzene. Without laying too much stress on the results, it seemed desirable to calculate the rise of freezing point with addition of water in the same way as had been done with benzene, methyl alcohol and water. The results thus obtained are given under the heading «Δ calc» in Table V. In Table VI are the formulas used in calculating these data.

TABLE VI

I $0.75 \log g - \log \Delta_1 = 0.255$
II $0.75 \log g - \log \Delta_2 = 0.230$
III $0.75 \log g - \log \Delta_3 = 0.065$
IV $0.75 \log g - \log \Delta_4 = 0.070$
V $0.75 \log g - \log \Delta_5 = 0.133$

There are two points to be noticed with respect to this table. The integration constants are not identical for all the solutions studied as was the case with methyl alcohol. The integration constants decrease, pass through a minimum and increase again with increasing concentration of ethyl alcohol. It therefore seems probable that with solutions containing anywhere from seventy-five to ninety-five grams of ethyl alcohol per hundred grams of benzene we should get the same phenomenon as with methyl alcohol. Conversely we should expect that with methyl alcohol a variation of the concentration in either direction would show an increase in the value of the integration constant.

From the data in Tables III and V it is possible to construct a series of isotherms showing qualitatively the way in which the concentration of alcohol and water must vary in order to keep the freezing point of benzene constant. This has been done and the results are given in Table VII where the concentrations of alcohol and water are expressed in grams of these two substances per hundred grams of benzene while the temperatures are measured from the freezing point of benzene as the zero point.

I had hoped to be able to express these isotherms quantitatively by a suitable application of the Mass Law; but this has not proved possible. The general form of the curves is such as to make it

TABLE VII

Temp. — 4°		Temp. — 6°	
Alcohol	Water	Alcohol	Water
28.2	0.0	63.3	0.0
75.5	4.2	75.5	0.95
94.7	7.0	94.7	3.4
122.7	14.0	122.7	8.0
Temp. —5°		Temp. —6.6°	
46.2	0.0	72.5	0.0
75.5	2.5	75.5	0.15
94.7	4.9	94.6	2.7
122.7	10.6	122.7	6.4

seem probable that different conditions prevail above and below —5°. While I am by no means prepared to state that this is the fact, it is certainly curious when taken in connection with the behavior of the system containing benzene and alcohol only.

I have also made a few measurements with crystallized cupric chlorid, benzene and water. Since cupric chlorid is insoluble in benzene and soluble in alcohol, addition of it should raise the temperature at which benzene first crystallizes. In Table VIII are the experimental data. The original solution contained *70.19* g alcohol per hundred grams of benzene. In the first column are grams of cupric chlorid per hundred grams of benzene; in the second, grams of water per hundred grams of benzene; in the third, the observed rise of freezing point; in the fourth, the rise due to the water, estimated from my other experiments; in the fifth, the difference

TABLE VIII

$CuCl_2$	H_2O	Δ	ΔH_2O	$\Delta CuCl_2$
1.29	0.35	+0.24°	+0.20°	+0.04°
2.98	0.80	0.61	0.42	0.19
5.18	1.39	1.28	0.68	0.40
8.68	2.33	1.99	1.05	0.94

between the third and the fourth columns or the rise due to the cupric chlorid.

Since the addition of water to a benzene-alcohol mixture decreases the effect of the alcohol in lowering the freezing point of the benzene, it is to be expected that the addition of benzene and water to alcohol will lower the vapor pressure of the alcohol more than the same number of reacting weights of benzene alone or of water alone. In other words we should expect that the vapor pressure of the alcohol would be decreased more by two solutes which were non-miscible than by the same concentrations of two which were mutually soluble. If we change from alcohol as solvent to some substance which can exist as solid phase at the temperature of the experiment we should expect to find the molecular depression due to either solute increased by the presence of the other when the two are non-miscible. This has been formulated by Abegg[1] as follows: The depression of the freezing point by two solutes is distinctly greater than the sum of the single depressions and can be calculated, by means of a single assumption, with sufficient accuracy». Although Abegg's experiments certainly justify this position, it seems to me probable that it will have to be modified somewhat before long. For the moment we will limit the discussion to the cases where the solutes are non-miscible. Abegg[2] found that

TABLE IX

	Δ		Δ
n/2 KBr	—1.710°	n/2 KBr	—1.710°
n C_2H_5OH	1.855	n CH_3COOH	1.756
Sum	3.565	Sum	3.466
Observed	3.902	Observed	3.619
n/2 KBr	—1.710	n/4 Li_2SO_4	—1.136
n NH_3	1.369	n CH_3COOH	1.756
Sum	3.079	Sum	2.892
Observed	3.156	Observed	3.169

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[1] Zeit. phys. Chem. **15**, 260 (1894).

[2] Ibid. **11**, 259 (1893)

with potassium bromid in presence of ethyl alcohol, acetic acid or ammonia the depression for the two substances was greater than the sum of the single depressions and that this was also the case with lithium sulfate and acetic acid. His data are given in Table IX. Under the heading «Observed» is the change of freezing point for the mixture.

While there is no doubt that the observed depression is greater than the sum of the single depressions and that the percentage differences agree qualitatively with what one might reasonably expect to occur, it must be admitted that these particular combinations are not ideal ones for bringing out the important part due to the relative solubilities of the three components. More suitable for my purpose are the experiments of Tanatar, Choina and Jozirew[1] upon salts in the presence of methyl alcohol, ethyl alcohol or acetone. In Table X are given the concentrations of their original solutions expressed in grams per thousand grams of water; the observed change of freezing point and the molecular depression K calculated from the formula:

$$\frac{M\Delta}{g} = K \text{ where M is the reacting weight.}$$

TABLE X

	Concentration	Δ	K
I	100 g C_2H_5OH	−4.00°	1.84
II	200 g C_2H_5OH	8.45	1.95
III	250 g C_2H_5OH	11.00	2.02
IV	100 g CH_3OH	5.3	1.70
V	200 g CH_3OH	10.7	1.71
VI	100 g CH_3COCH_3	3.2	1.86
VII	200 g CH_3COCH_3	6.4	1.86
VIII	300 g CH_3COCH_3	9.2	1.81

All three solutes are fairly «normal» even at these concentrations, the variations from the theoretical value not exceeding ten percent. In Table IX are the results obtained by adding various substances to these eight solutions. In the first columns are the

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[1] Zeit. phys. Chem. **15**, 124 (1894); Zeit. anorg. Chem. **9**, 229 (1895); **12**, 229 (1896).

names and concentrations of the substances, except that *n* is used in the sense of one reacting weight in one thousand grams of water instead of one liter of the solution. Under K_0 are the molecular depressions for these substances at these concentrations in pure water. Under K_1 — K_5 are the molecular depressions for the same substances in the first five solutions of Table X, the freezing points of those solutions being taken as zero. Thus a solution containing one-half a reacting weight of sodium chlorid, two hundred and fifty grams of ethyl alcohol and one thousand grams of water froze at — 14°C. Since the same solution, minus the sodium chlorid, froze at — 11°, the depression due to the salt is three degrees and the molecular depression K_3 is six.

TABLE XI

	K_0	K_1	K_2	K_3	K_4	K_6
n NaCl	3.51	4.45	5.40	5.90	4.82	5.1
n/2 NaCl	3.50	4.60	5.60	6.0	5.0	5.6
n KCl	3.36	4.25	5.25	5.30	4.0	4.6
n/2 KCl	3.30	4.40	5.50	6.0	4.2	5.2
n/2 KNO_3	3.0	3 70				
n KBr	3.51	4.10	5.0	5.15	3.8	4.4
n/2 KBr	3.50	4.40	5.10	5.40	4.0	4.2
n KI	3.52	4.00	4.45	4.40	3.9	4.4
n/2 KI	3.52	4.20	4.60	4.30	4.2	5.2
n Sugar	1.85	2.90	3.65	3.35	2.85	3.6
n/2 Sugar	1.85	2.90	3.80	3.90	3.24	3.8

We see that there is a very large increase in the molecular depression due to the presence of alcohol, ethyl or methyl; that this increase is greater the more alcohol is present and that it increases as the ratio of alcohol to salt increases so that the values for half normal salt solutions are, with one exception, larger than those for the normal solutions. We see also that cane sugar shows the same abnormal behavior as the salts, not because it is an electrolyte for it is not; but because it is precipitated from aqueous solution by alcohol.

Since acetone possesses less precipitating power than either ethyl or methyl alcohol we should expect to find somewhat lower values for the molecular depression when this liquid replaces alcohol in the solution. In Table XII the date under the headings $K_6 - K_8$ refer to the results obtained when starting from the last three solutions of Table X.

TABLE XII

	K_0	K_6	K_7	K_8
NaCl	3.51	4.15	4.65	5.20
KCl	3.36	3.9	4.35	4.75
KBr	3.51	3.7	3.83	4.10
KI	3.52	3.3	3.10	2.80
Sugar	1.85	3.3	3.10	2.80

The values are lower than the corresponding ones in Table XI and with potassium iodid we actually get a decrease in the constant instead of an increase while with sugar we have the value apparently passing through a maximum.

I have made a few measurements with alcohol, sugar and water in order to verify these results of Tanatar's for other concentrations. In Table XIII are the data for sugar and water, alcohol and water. The concentrations are expressed in reacting weights per thousand grams of water. Under K are the molecular depressions. In Table XIV are the values for sugar in a solution containing *0.78* reacting weights of alcohol per thousand grams of water. Under K_1 and K_0 are the molecular depressions with and without alcohol, the latter being taken from Table XIII. The values for K_1 are larger than those for K_0 until we come to the last determination. In Table XV are the data for alcohol in solutions containing *0.28* and *0.77* reacting weights of sugar respectively,

TABLE XIII

Sugar	Δ	K	Alcohol	Δ	K
0.07	—0.13°	1.86	0.199	—0.37°	1.86
0.20	0.41	2.05	0.442	0.83	1.88
0.37	0.76	2.06	0.606	1.14	1.88
0.64	1.36	2.12	0.854	1.58	1.85
0.79	1.73	2.19	1.150	2.09	1.82
0.96	2.09	2.18			
1.55	3.55	2.29			

TABLE XIV

Alcohol = 0.78

Sugar	Δ	K_1	K_0
0.16	—0.38°	2.38	1.96
0.44	1.06	2.41	2.08
0.68	1.52	2.24	2.14
0.79	1.73	2.19	2.19

TABLE XV

Sugar = 0.28				Sugar = 0.77			
Alcohol	Δ	K_1	K_0	Alcohol	Δ	K_1	K_0
0.25	—0.49°	1.96	1.86	0.33	—0.75°	22.7	1.87
0.86	1.68	1.93	1.85	0.78	1.67	21.4	1.88
1.30	2.56	1.97	1.81	1.28	2.85	21.0	1.86
				1.79	3.65	20.4	1.80

per thousand grams of water. With more sugar we get an increasingly abnormal value for the molecular depression.

It occurred to me that with water, alcohol and a salt, one should obtain different results when the salt was soluble in alcohol and when it was not. To test this I made some measurements with cupric chlorid and with barium chlorid the results of which are given in Table XVI. The concentrations are reacting weights (not equivalents) per thousand grams of water.

TABLE XVI

Alcohol = 0.84			Alcohol = 1.02		
$CuCl_2$	Δ	K	$BaCl_2$	Δ	K
0.12	—0.67°	5.58	0.09	—0.47°	5.22
0.38	2.12	5.58	0.31	1.66	5.36
0.62	3.52	5.68	0.46	2.53	5.50
0.83	4.75	5.72	0.54	3.00	5.56

To my surprise there was either no difference to be detected between the two salts or, if anything, cupric chlorid was more abnormal than barium chlorid. I am not able to offer a satisfactory explanation of this phenomenon. It may be that the dissociation of the cupric chlorid is affected very slightly by the alcohol and that of barium chlorid a great deal; but that is purely hypothetical and further investigation will be necessary in order to clear up this point.

We have now considered the two cases where the solid phase is one of the two non-miscible components and the one where it is neither of them. The third case that occurs experimentally is the one in which each of the components is miscible to a certain extent with either of the others. It has already been stated that Abegg makes no distinction between this case and the second in so far as the change of the freezing point is concerned. In support of this view we have Abegg's own measurements with glycerol or acetone and aqueous alcohol. Here the difference between the total depression and the sum of the partial depressions is practically the same percentage of the total change as in the case of sugar and methyl alcohol. This is confirmed by the experiments of Tanatar with acetone and ethyl alcohol. On the other hand Abegg finds that with potassium acetate and acetic acid in aqueous solution the sum of the single depressions exceeds the observed depression slightly. Tanatar finds that the molecular depression of methyl alcohol in water is unchanged by presence of acetone and that acetic acid gives the same values when methyl or ethyl alcohol is present and decreasing values in presence of acetone. In benzene solutions we get much less than the theoretical values. In Tables XVII and XVIII are some data illustrating this point.[1] In Table XVII are the changes of the freezing point and the molecular depressions caused by adding the specified quantities of ethyl alcohol, methyl alcohol or acetone to one thousand grams of benzene. In Table XVIII are the molecular depressions obtained by adding one reacting weight of the substances mentioned to the solutions given in Table XVII. The method of tabulating is the same as in Tables X and XI. The values under K_0 were not given by Tanatar and were taken from Beckmann,[2] Auwers[3] and Ostwald[4] and are therefore to be considered

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[1] Tanatar, Choina and Jozirew, Zeit. anorg. Chem. **12**, 229 (1896).

[2] Zeit. phys. Chem. **2**, 715 (1888).

[3] Ibid. **12**, 689 (1893).

[4] Lehrbuch I, 750.

only as rough approximations when applied to these particular experiments.

TABLE XVII

	Concentration	Δ	K
I	100 g C_2H_6OH	−3.1°	1.43
II	200 g C_2H_5OH	4.3	0.99
III	100 g C_3H_8OH	3.3	1.06
IV	200 g CH_3OH	4.2	0.67
V	100 g CH_3COCH_3	7.7	4.59
VI	200 g CH_3COCH_3	13.0	3.88

TABLE XVIII

	K_0	K_1	K_2	K_3	K_4	K_5	K_6
CH_3OH	1.70	0.50	0.30			0.60	0.37
Camphor	4.94	4.45		4.15	4.35	4.4	4.37
$CHCl_3$	5.11	4.53	4.20	4.40	4.10		
CH_3COOH	2.35	1.13	1.00	0.70	0.70	0.12	0.22
C_2H_5OH	1.98			0.45	0.40	0.62	0.37

With camphor and chloroform there is a marked though not extraordinary decrease in the value of the molecular depression. With the two alcohols and acetic acid the diminution is enormous. Of course with these latter it is always possible to speak of increased polymerization ; but that does not seem to be of any real advantage and is not applicable to chloroform and camphor. It seems to me that these data are sufficient to warrant us in discarding Abegg's generalization with regard to the freezing points of ternary mixtures. These data were not known at the time that Abegg wrote his paper or he would doubtless have modified his statement somewhat. Curiously enough it apparently has not occurred to him or to any one else that his position is not compatible with that of Nernst on the boiling points of ternary mixtures.[1] In considering the rise of the boiling point when a non-volatile substance is added to a mixture of two volatile components, Nernst makes the assumption that «the solute distributes itself to a certain extent between the two

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[1] Zeit. phys. Chem. **11**, 1 (1893).

solvents». Supposing this true, the change in the vapor pressure of one of the solvents can not be as great as if the third component were dissolved in it alone and under these circumstances the freezing point of the solvent will not be lowered as much by the addition of the third component to the mixture as by the addition of the third component to the pure solvent. In other words, the depression of the freezing point for the mixture will be less than the sum of the single depressions, a view which is supported experimentally by the measurements of Tanatar. It must, however, be kept in mind that while this way of looking at the subject is undoubtedly the correct one, there are some very serious difficulties which call for explanation. Interpreting Abegg's experimental results from this point of view we are forced to the conclusion that alcohol and water are to be considered as two non-miscible liquids in a consolute liquid, water, a result which will be accepted by no one.

The facts brought out in this paper make it impossible to accept an assumption recently advanced.[1] Luther says: «The experimental verification of the van 't Hoff laws has shown that, for the same molecular concentration in the same solvent, the vapor pressure (of the solvent) is independent of the nature of the solute. Considering these experimental facts to apply to mixed solvents, a view apparently justified by Roloff's experiments, we must expect that the pressure and composition of the vapor above such solutions will be a definite function of the relative concentrations of the two liquids and of the molecular concentration of the solute but will be independent of the nature of the latter». If we take the case where two of the components are non-miscible as coming under this head, Roloff's experiment with potassium chlorid, acetic acid and water, Freyer's experiments with alcohol, sugar and water and my own measurements with benzene, water and alcohol, benzene, cupric chlorid and alcohol show the inaccuracy of this view conclusively. These instances were undoubtedly not what Luther had in mind and, if asked to define his position more closely, he would probably limit his remarks to mixtures in which the relative concentrations were such that any two of the components would form a homogen-

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[1] Zeit. phys. Chem. 19, 542 (1896).

eous liquid phase without the third. If worded this way there are no experimental data sufficient to prove or disprove this view; but the measurements of Tanatar already cited make it seem very probable that the composition of the vapor will depend upon the relative solubility of the third component in the two solvents.

The results of this paper may be summed up as follows:

1. Addition of a substance to a binary solution in equilibrium with a solid phase raises the freezing point if the substance added be non-miscible with the component appearing as solid phase.

2. The freezing point is lowered if the substance added be non-miscible with the component which does not appear as solid phase and this lowering is greater than if the substance were added to the pure solvent.

3. When the three components are miscible the sum of the single depressions is usually greater than the depression for the mixture; but this is not always true owing to disturbing conditions which are not yet defined.

Cornell University

ON POTASSIUM LEAD IODID

BY J. M. TALMADGE

In a paper on the isothermal curves for double salts Schreinemakers[1] showed that the part of the isotherm along which the double salt is solid phase may have three forms: one such that by concentration of the solution there is always a precipitation of double salt—a second such that the reverse takes place and a third such that there is a first precipitation and then solution of the double salt. In the third a reversal of the phenomenon takes place at that point of the isotherm at which a line through the origin becomes tangent to the curve. (This refers to the diagram in which the parts of one salt and of the other in a constant quantity of water are taken as the coordinates). After a short digression about the two forms of that part of the isotherm along which one of the components is solid phase he goes on: « As third case it is also possible with double salts that concentration of the solution is always accompanied by solution of the double salt. This case should occur with the double salt PbI_2KI2H_2O at ordinary temperatures. As a matter of fact I have found this phenomenon as well as the reverse one (precipitation of double salt by dilution) confirmed experimentally ». While the more important points are thus outlined by Schreinemakers, the general relations would have been clearer if he had made a few more subdivisions. Some qualitative experiments of my own have convinced me that Schreinemakers's statement in regard to the potassium lead iodid is not correct as it stands or, more properly speaking, is incomplete. The double salt does dissolve on concentration; but only under certain conditions. Under others it precipitates. For this reason it has seemed worth while to supplement Schreinemakers's paper by a somewhat more extended treatment of the behavior of a double salt on addition or subtraction of water at constant temperature, limiting the discussion to the case in which the double salt is decomposed by water and each salt increases the solubility of the other. Let A and B be the two salt components and AB the double salt. The double salt and either or both of

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[1] Zeit. phys. Chem. **11**, 83 (1893).

the components may contain water of crystallization. The only limitation is that no dehydration shall occur along the isotherm.

We will adopt the Schreinemakers form of diagram, the amount of the component B in a constant quantity of water being measured along the axis of abscissas and the amount of the component A in a constant quantity of water along the axis of ordinates. The double salt is decomposed by water with precipitation of A. If the point K represents the solubility of pure A, H the solubility of pure B, C the concentration of the solution in equilibrium with A and $\overline{AB}$ as solid phases and D the concentration of the solution in equilibrium with AB and B as solid phases we shall have A as solid phase along KC, AB along CD and B along DH. The field OKCDHO represents unsaturated solutions, no solid phase being possible, while beyond the curves KCDH the solution phase does not represent a state of stable equilibrium. We have two cases to distinguish:

I. The ratio of A to B is greater at D than at C.
II. The ratio of A to B is less at D than at C.

Under these two main heads come the following subdivisions:
Ia. Neither of the lines OC and OD cuts CD in two points.
Ib. The line OD cuts CD in two points.
Ic. The line OC cuts CD in two points.
IIa. Neither of the lines OC and OD cuts CD in two points.
IIb. The line OD cuts CD in two points.
IIc. The line OC cuts CD in two points.

The schematic diagrams for these six cases are presented in the six cuts.

On adding water to any solution in equilibrium with a solid phase the system passes from the point in the diagram representing that concentration along the straight line connecting that point with the origin O. If this brings the system into the field OKCDHO the solid phase will dissolve; if this brings the system into the field for supersaturated solutions more of the solid phase will precipitate. On withdrawing water, the system tends to pass along the line from the origin through the point representing the concentration, moving away from the origin.

Ia. Addition of water to any solution on the line CD[1] will cause precipitation of the double salt, the system passing along the curve DC until the point C is reached when the double salt changes into the salt A. The solution then passes along CK with solution of A until at some point on this curve the whole of this salt disappears leaving an unsaturated solution. On concentrating any solution represented by a point on CD, the double salt will dissolve and the system will move along CD in the direction of D. If the amount of double salt is very large relatively to the quantity of the solution, the point D will be reached before the double salt has disappeared. On further concentration the salt B will separate and the solution will evaporate to dryness without change. If there is relatively little of the double salt, it will disappear before the concentration D is reached and we shall have an unsaturated solution. When this has lost a certain amount of water, the salt B will precipitate, the system will move along HD, where the double salt will appear and the solution will evaporate to dryness without change of concentration since the system has no degrees of freedom. This is probably the diagram which Schreinemakers had in mind when he said that the double salt may always dissolve when the solution is concentrated and he would therefore place lead potassium iodid at 20° in this subdivision.

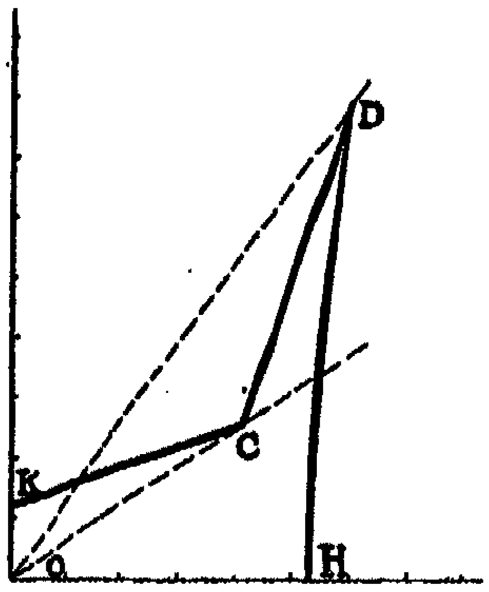

FIG. Ia

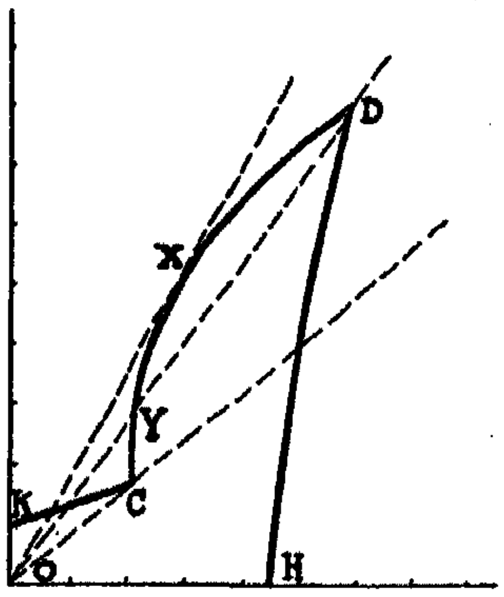

FIG. Ib

Ib. If X is the point at which a line through O becomes tangent to the curve, adding water to any solution represented by a

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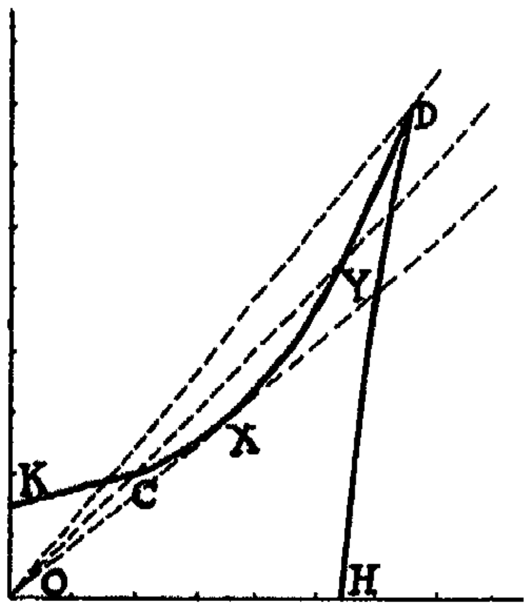
[1] It is immaterial whether CD be convex or concave to the X axis.

point on DX will cause the double salt to go into solution, the system moving along the curve towards X. If there is a relatively large amount of double salt, it will not disappear before the concentration corresponding to X has been reached. On further addition of water there will be precipitation of double salt and the system will pass along the curve to C where the double salt will be decomposed by water just as in Ia. Evaporating at constant temperature the system will pass along the curve CD if there is an excess of double salt, this compound dissolving along C and precipitating along D. At D the solution will go to dryness without change. If there is so little of the double salt that it disappears before the concentration Y is reached, the solution will remain unsaturated until the salt B precipitates at a concentration represented by a point on HD. The system will pass along HD with precipitation of B until D is reached when it will go to dryness without change of concentration. If the double salt disappears somewhere between Y and X nothing will precipitate until the corresponding point on XD is reached when the double salt will precipitate and the system will pass along the curve to D. It will be shown later that potassium lead iodid at 20° offers an instance of this sort.



FIGS. Ic

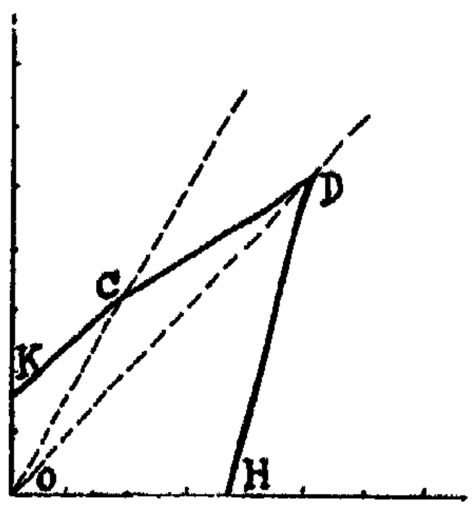


FIG. IIa

Ic. This is the reverse case to Ib. Addition of water to any solution represented by a point on the curve DX causes precipitation of the double salt, the system moving toward X. Addition of water to any solution represented by a point on XC causes solution of the double salt, while the system moves toward C. It depends on the relative masses of the phases whether or not an unsaturated solution is formed before reaching the point C. Starting from any point on CX and evaporating at constant temperature will cause precipitation of the double salt, the system passing along CX. From X to D there will be solution of the double salt and possible formation of an unsaturated solution. If this latter is formed, salt B will eventually precipitate and the system will pass back along HD to D.

IIa. Addition of water will always cause the double salt to dissolve and evaporation will always make it precipitate.[1] This is the reverse behavior from that observed under Ia. The experiments of Schreinemakers show that the isotherm for the iodids of lead and potassium in aqueous solution at 165° is of this type.

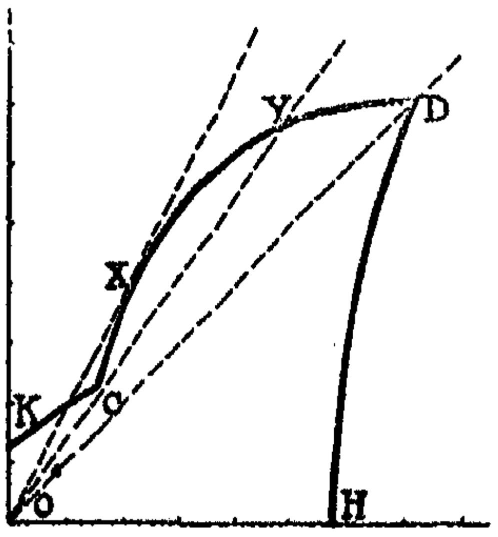


FIG. IIb

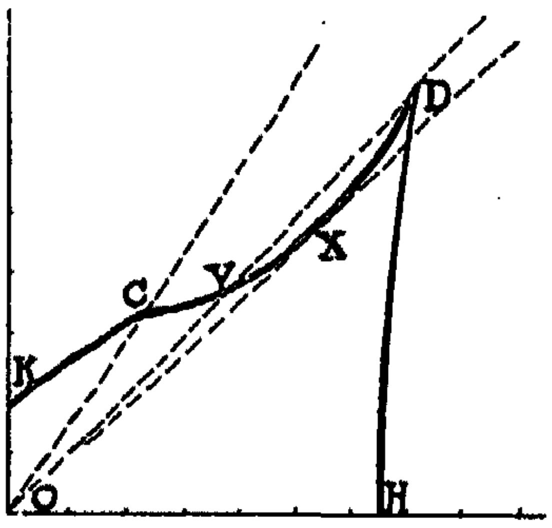


FIG. IIc

IIb. From D to X addition of water causes solution of double salt, from X to C precipitation. If the double salt disappears before Y is reached, no further addition of water will produce a precipitation. If it disappears between Y and X, further addition of water will make the double salt precipitate. Evaporation will cause the double salt to dissolve between C and X and to precipitate between X and D. If the double salt disappears before the system reaches X it will be precipitated on further evaporation.

IIc. Addition of water precipitates the double salt from D to X and dissolves it from X to D. Withdrawal of water precipitates the double salt from C to X and dissolves it from X to D. If an unsaturated

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[1] It is immaterial whether CD be convex or concave to the X axis.

solution be formed while the system is passing along XD, the salt B will precipitate on further evaporation.

On allowing a certain solution from which the double iodid of lead and potassium, PBI_2KI2H_2O had separated, to evaporate spontaneously I noticed that the crystals disappeared and that addition of water brought them back again just as described by Schreinemakers. Further evaporation, however, caused them to reappear, thus showing that the system was to be classified under Ib instead of under Ia. The precipitation of the double salt by water is a very striking experiment. In order to know what proportions of the three components give a clear solution from which the double salt precipitates either on concentrating or diluting the solution it will be necessary to determine the course of the isotherm. If one merely wishes to show the precipitation and subsequent decomposition of the double salt by water, one can do this without the trouble of making weighings by taking a saturated solution of potassium iodid, adding lead iodid till the double salt begins to separate, decanting the solution and adding water.

At about 70° the line OC passes through D. At temperatures below 70°, D lies above the line OC and below it at temperatures above 70°. Whether the curve CD is convex or concave to the X axis at 70° is not known; but it is probable that it is one or the other and not a wavy line. At 20° the curve is certainly concave and at 165° equally certainly convex. At 100° some experiments which I made showed that the system came under the head IIa because there was continued precipitation of the double salt on evaporation; but this proves nothing in regard to the convexity or concavity of the curve. One prediction we may make safely. If the curve is concave at 70° we shall have a system coming under Ib at 69° and IIb at 71°. If the curve is convex at 70° we shall have a system coming under Ic at 69° and IIc at 71°. Under any circumstances we have in the potassium lead iodid a double salt which gives us at different temperatures three out of the six forms of the curve CD which have been discussed in this paper. The work has been done with the assistance of Professor Bancroft.

Cornell University

NEW BOOKS

Contributions to the Analysis of the Sensations. *Ernst Mach; translated by C. M. Williams. ix and 208 pages. The Open Court Publishing Co.; Chicago, 1897. Price $1.25.* Everyone who cares in any way for physical science, beyond having a concern for bare details, must be profoundly interested by Mach's Analysis of the Sensations. It gives in outline a philosophy of science which is brief, clear and deeply satisfying. The author is convinced that the foundations of science as a whole, and of physics in particular, await their next great elucidations from biology and especially from the analysis of the sensations; the present work assembles the results of the researches into which he has been led by this conviction during the past thirty years. His chapters on the detailed study of the relation between feeling and its physiological counterpart develop the idea that as many physicochemical neural processes are to be assumed as there are distinguishable qualities of sensation, an idea which is made to illuminate remarkably our varied sensations of space, time and sound. The treatment is arranged under the successive general heads: Antimetaphysical Introduction; the Chief Points of View; Space Sensations of the Eye; Sensations of Sight, of Time and of Tone; Influence of these Researches upon the Conception of Physics; Facts and Mental Symbols. The author's topic is nothing less than the whole basis of science, and it is handled in a consistent, thorough and remarkably independent manner. A general interest, as against a special one, is aroused in particular by the opening and the closing chapters of the work, where the point is especially made that our world is a complex of interrelated sense elements. The following passage is characteristic:—

« Bodies do not produce sensations, but complexes of sensations (complexes of elements) make up bodies. If, to the physicist, bodies appear the real, abiding existences, whilst sensations are regarded merely as their evanescent, transitory show, the physicist forgets, in the assumption of such a view, that all bodies are but thought-symbols for complexes of sensations (complexes of elements). Here, too, the *elements* form the real, immediate, and ultimate foundation, which it is the task of physiological research to investigate. By the recognition of this fact, many points of psychology and physics assume more distinct and more economical forms, and many spurious problems are disposed of.

» For us, therefore, the world does not consist of mysterious entities, which by their interaction with another, equally mysterious entity, the ego, produce sensations, which are alone accessible. For us, colors, sounds, spaces, times, . . . are the ultimate elements. . . . The aim of all research is to ascertain the mode of connexion of these elements ».

Through the present English version of this book the Open Court Company has conferred a considerable benefit upon English speaking students of all branches of natural science. The translation has been carefully made, the volume is well illustrated and indexed, and it has been supplied by the author with extensive new notes and appendices and a preface. There is no work known to the writer which in its general scientific bearing is more likely to repay richly thorough study. We are all interested in nature in one way or another, and our interests can only be heightened and clarified by Mach's wonderfully original and wholesome book. It is not saying too much to maintain that every intelligent person should have a copy of it,—and should study that copy. *J. E. Trevor*

Der erste und zweite Hauptsatz der mechanischen Wärme-Theorie und der Vorgang der Lösung. *Robert Pauli. Octavo, 115 pages. M. Krayn; Berlin, 1896.* The present small volume is announced to be «an energetic theory of the chemical molecule»; its successive portions are devoted to Energy, Thermodynamics of a molecule, the Second Law of Thermodynamics, Solution, and Dependence of Solution Pressure upon Temperature.

Two things seem to have been attempted, a polemic against Ostwald's idea of the substantiality of energy, and a recapitulation of the principles of thermodynamics. Neither of them is well done; the polemic is abusive and brings up no important points, the thermodynamics is ridiculously superficial and fragmentary. The author writes of the «crystallized chemical molecule» (p. 47); that though the scientific distinguishing between bodies is wholly of an ‹energetic› nature yet «we must hold fast to the atoms» (p. 13), that «over 95 percent of all chemical reactions are reactions of chemical molecules dissolved in water» (p. 47), and many more absurdities. The many typographical errors keep the mechanical execution of the book down to the level of its scientific character.

J. E. Trevor

Elektrotechnische Bibliothek. XLVI. Elektricität direkt aus Kohle. *E. de Fodor. Small octavo, xii and 306 pages. A. Hartleben: Wien, 1897. 3 marks; bound, 4 marks.* This is a very compact, useful little book though the title is more catching than accurate. The author has undertaken to give a brief statement of our knowledge in regard to the production of electricity directly or indirectly from coal without steam power. The subject is treated under the headings: carbon in the voltaic cell; carbon elements with melted electrolytes; two metal electrodes in melted electrolytes; the Borchers gas cell; thermopiles; other attempts to convert heat into electricity; conversion of chemical into electrical energy. The most interesting parts of the book are those on the Jacques cell, on the Borchers cell and on the improvements in thermopiles. It is interesting to note the contemptuous way in which the author refers to Jacques, as compared with his tone in regard to Borchers, although neither of the two cells is worth anything so far as one can judge from the evidence. One very extraordinary fact comes out in the book,—that no one in all this time has made any experiments to determine the electrochemical equivalent of carbon in any of the reactions. The book is to be recommended to everyone interested in the subect.

Wilder D. Bancroft

Elektrotechnische Bibliothek, XLVII. Angewandte Elektrochemie. *F. Peters. Vol. I. Small octavo xiv and 338 pages. A. Hartleben; Wien, 1897. Price 3 marks; bound, 4 marks.* This volume—the first of three on applied electrochemistry—is devoted to batteries and accumulators, In it the reader will find brief descriptions of the different forms of the Leclanché, Daniell, Grove, Bunsen and Cupron cells, to mention a few only. Other chapters treat of normal cells, gas cells and thermopiles, while more than one-third of the book is given up to a discussion of accumulators. It is a book to refer to for matters of detail, being a dictionary in all save arrangement.

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 which bear upon any phase of Physical Chemistry.

General

Studies on the Relations among the Atomic Weights. *J. R. Rydberg. Zeit. anorg. Chem.* **14**, *66* (*1897*). An analytical study of the atomic weights. Like so many others the author comes to the conclusion that the tendency to approach multiples can not be fortuitous and, like every one else—except Hinrichs,—he stops there. Either the atomic weights, as at present determined are nearly right or they are not. Until it is shown that they are not and why they are not, it is a waste of time to apply the theory of probabilities to the periodic system. There is nothing so fatal to progress as to be afraid of one's conclusions and yet to cling to them.

W. D. B.

Classification of the Chemical Elements. *Lecoq de Boisbaudran. Comptes rendus,* **124**, *127* (*1897*). Remarks of the usual kind on the differences between the atomic weights of adjacent and non-adjacent elements. *W. D. B.*

More about the Relations between the Molecular Weights in Liquids and Solids. *U. Alvisi. Rend. Accad. Lincei,* (*5*) **6**, *77* (*1897*). The author believes that «in equal volumes there are equal numbers of equivalent weights of matter». He uses colligative» in the sense of «additive». *W. D. B.*

On the Analogies in Composition of the Salts of Calcium, Strontium and Barium. *J. H. Kastle. Am. Chem. Jour.* **19**, *281* (*1897*). From a study of 141 acids, of which the barium, strontium and calcium salts have been prepared, the author draws the conclusion: «Of the calcium, strontium and barium salts of any acid, all or two of the salts of these metals will be found to be analogous in composition». There were 28 apparent exceptions. These results overthrow the hypothesis of Lenssen that strontium and barium are each more like the other than like calcium. *W. D. B.*

Remarks on the Specific Heats and Atomic Constitutions of the Elementary Gases. *M. Berthelot. Comptes rendus*, **124**, *119* (*1897*). After making the assumption that every one believes that the ratio of the two specific heats of gases must be *1.41*, the author points out that for monatomic gases we have *1.66*; for diatomic gases *1.41*; for diatomic gases which dissociate below 2000°, such as the halogens, *1.30*; for tetratomic gases, *1.175*. The interesting feature of the paper is that the author evidently believes that there is something original in it. *W. D. B.*

On the Specific Heat at Constant Volume of the Hydrocarbons. *S. Pagliani. Nuovo Cimento*, (*4*) **4**, *146* (*1896*). From the data of Schiff the author has calculated the specific heat at constant volume and the ratio of the specific heats at constant pressure and volume for the vapors of benzene, toulene, xylene, cymene. He shows that this ratio is less than *1.4* and decreases with the increasing molecular weight of the substance. *W. D. B.*

On the Determination of the Water Equivalent of Thermometers for Calorimetric Work. *A. Sozzani. Nuovo Cimento*, (*4*) **5**, *135* (*1897*). The author points out that if one knows the specific heats of the mercury and glass in the thermometer one can calculate the specific heat of the instrument provided the specific gravities of the glass and the mercury are also known. *W. D. B.*

An Apparatus for Showing Experiments with Ozone. *G. S. Newth. Jour. Chem. Soc.* **69**, *1298* (*1896*). By twisting a stopper, a tube containing turpentine or potassium iodid is crushed without changing the level of the liquid in the manometer. *W. D. B.*

Vaporization of a Liquid in a Confined Space. *P. Lami. Nuovo Cimento*, (*4*) **5**, *27* (*1897*). For lecture experiments the author uses a test tube into which passes a siphon tube having a stop-cock at the outer end. By a little simple manipulation it is possible to bring ether and mercury into the test tube in such wise that the mercury is driven part way up the siphon tube by the vapor pressure of the ether. *W. D. B.*

On a Thermometer for very low Temperatures and on the Thermal Expansion of Petroleum-ether. *F. Kohlrausch. Wied. Ann.* **60**, *463* (*1897*). Petroleum-ether is still fluid though viscous at − 190°. Glass thermometers were calibrated by filling with mercury, and then filled with the petroleum-ether and closed. The temperatures of the baths, − 50°, − 80° and − 190° were measured by a constantin-iron couple which had been compared with the hydrogen scale. Tables of the expansion are given. At − 188° the volume is only $^4/_5$ of that at 0°. The author has found no simple formula for representing the results. Similar but less complete experiments were made on amylene. *E. B.*

Monovariant Systems

A Property of the Heat of Vaporization of Liquefied Gases. *G. Bakker. Jour. de Phys.* (*3*) **6**, *137* (*1897*). With CO_2 and N_2O Mathias has found that for the heat of vaporization r, at the critical point, $dr/dT = -\infty$. To show this to be a general property of the heat of vaporization Bakker starts from the vaporization equation

$$T\frac{dp}{dT} = \frac{r}{s - \sigma}$$

which becomes the indeterminate $\frac{o}{o}$ at the critical temperature. Still, by the theorem of L' Hôpital,

$$T\frac{dp}{dT} = \frac{dr}{dT} \Big/ \left(\frac{ds}{dT} - \frac{d\sigma}{dT}\right)$$

where the denominator of the second member may be shown to be $-\infty$; so, since the first member remains finite, $dr/dT = -\infty$, as found. The same proposition is shown to hold for the inner heat of vaporization $\rho = r - p(s - \sigma)$. [These results were advanced by the author in 1892 in a similar paper in the Zeit. phys. Chem **10**, *558*.] *J. E. T.*

On the Variation of the Temperature of Fusion with Pressure. *R. Demerliac. Jour. de Phys.* (*3*) **6**, *126* (*1897*). The temperatures are measured by the bolometer; the metallic manometer is graduated at the Eiffel tower. Between 1 atm and 10 atm benzene, paratoluidin and α-naphthylamine follow Clapeyron's formula very exactly. For great pressures (up to 450 atm) dT/dp approaches zero and T approaches a horizontal asymptote, p being the abscissa of the curve. For all three substances the experimental results are accurately represented by hyperbolas. The author does not state how he has determined the heat of fusion and the change of volume in fusion. He has found these, apparently, only for normal pressure, and Clapeyron's equation ceases to have a meaning if we have to use in it data referring to different states of pressure. The article is, in substance, a repetition of two notes in the Comptes rendus, **122**, 117 (1896), and **124**, 75 (1897); see this Journal **1**, 441. *E. B.*

The Influence of the Electrical Condition of a Liquid Surface on the Heat of Vaporization of the Liquid. *E. Fontaine. Jour. de Phys.* (*3*) **6**, *16* (*1897*). Admitting that during evaporation the molecules escaping from the surface do not carry any charge with them, the author shows by means of a cycle that the heat of vaporization for a given temperature is increased by electrification. No experimental test of the statement is given. *E. B.*

On Certain Peculiarities of the Curves of Solubility. *H. Le Chatelier. Zeit. phys. Chem.* **21**, *557* (*1896*). In a valuable memoir published in 1888, *Recherches sur les Equilibres chimiques*, page 138, the author has established a general formula connecting solubility with temperature. In the present paper he sets up an analogous expression:

$$i\frac{dc}{c} = 500\,L\,\frac{dt}{t^2} \qquad (1)$$

and applies it to the case where a solid substance, A_mB_n, (for example a double salt or an alloy) is in equilibrium with a liquid phase consisting of A_mB_n mixed with variable quantities of A and B (the single salts or metals respectively).

“In equation (1)

» c is the concentration of the *undissociated* substance $[A_mB_n]$ in the solution ; c is measured by the ratio of the number of molecules of the compound to the total number of molecules in the mixture.

» i is a factor which is proportional to the expression $\frac{c}{f}\frac{df}{dt}$ in the formula representing the lowering of the vapor tension with increasing concentration.

» If the formula of a chemical compound is A_mB_n, the following relation exists (according to van 't Hoff) between the concentration of the compound in the solution, and the concentrations c' and c'' of its components :—

$$i\frac{dc}{c} = mh\frac{dc'}{c'} + nj\frac{dc''}{c'} \qquad (2)$$

» Further, by definition of the term ‹ concentration ›

$$dc = -(dc' + dc'') . \qquad (3)$$

» At the maximum temperature of the curve of fusion [axes t and c] dt is equal to zero, and consequently [by equation (1)]

$$dc = o. \qquad (4)$$

» From this there follows :

$$\frac{c'}{c''} = \frac{m}{n}\cdot\frac{h}{j}\,. \qquad (5)$$

» In general, $\frac{h}{j}$ is different from unity, and consequently the quotient $\frac{c'}{c''}$ from $\frac{m}{n}$. In other words : at the maximum temperature of fusion the composition of the melted mixture is different from that of the chemical compound. »

This conclusion is in contradiction of a theorem of Gibbs, which was deduced without appealing to any specialized theory of solution. « For a given pressure the temperature of two coexisting phases is a maximum or a minimum when the composition of both phases is the same », *Thermodynamische Studien*, p. 118. The discrepancy appears to have its origin in the interpretation of equation (5) above. The equation

$$i\frac{dc}{c} = mh\frac{dc'}{c} + nj\frac{dc''}{c''} \qquad (2)$$

or, in the form adopted by Guldberg and Waage

$$c' = kc_{\prime}^{mh}c_{\prime\prime}^{nj}$$

holds only for reactions expressed by the chemical equation

$$i(A_mB_n)_{\frac{1}{i}} \rightleftarrows mhA_{\frac{1}{h}} + njB_{\frac{1}{j}}$$

that is, for reactions between substances whose molecular weights are the $\frac{1}{i}, \frac{1}{h}, \frac{1}{j}$ -*th* part respectively of those represented by the formulae A_mB_n, A and B. Consequently the letters c' and c'' in equation (5) refer to the number of molecules of $A_{\frac{1}{h}}$ and $B_{\frac{1}{j}}$ respectively in the solution, and $\frac{mh}{nj}$ is the ratio in which these substances unite to form the solid A_mB_n.

The following calculation of a general case will also serve to show that the methods of the modern theory of solution lead to the same conclusion as the less specialized argument of Gibbs referred to above.

Let the solution which is in equilibrium with the solid phase A_xB_y contain molecules of the following seven kinds viz.: A_xB_y (a double salt, for instance) A and B (its components) and a, α, b, β, (products of the electrolytic dissociation of the latter). To prevent unnecessary complications let the ions a and α have the same valency; similarly with b and β. From the results of a quantitative chemical analysis the composition of the mixture might be calculated in terms of a and b.

Corresponding to the are the

3 chemical equations	*3 Guldberg and Waage equations*
$A_xB_y \rightleftarrows xA + yB$	$A_xB_y = KA^xB^y = ka^{2mx}b^{2ny}$
$A \rightleftarrows ma + m\alpha$	$A = k_1a^m\alpha^m = k_1a^{2m}$
$B \rightleftarrows nb + n\beta$	$B = k_2b^n\beta^n = k_2b^{2n}$

and at equilibrium the relative numbers of the various kinds of molecules in the solution are :—

Formulas:	A_xB_y	A	B	a	α	b	β
Numbers:	$ka^{2mx}b^{2ny}$	k_1a^{2m}	k_2b^{2n}	a	a	b	b

Thus Le Chatelier's equations (3) and (4) become:

$$ka^{2mx}b^{2ny} + k_1a^{2m} + k_2b^{2n} + 2a + 2b = const. \qquad (3a)$$

$$\partial(ka^{2mx}b^{2ny}) = 0 \qquad (4a)$$

whence by differentiation and transformation :—

$$\frac{mx}{ny} = \frac{mk_1a^{2m} + a}{nk_2b^{2n} + b} \; . \qquad (5a)$$

Consequently under the conditions assumed, the ratio found by chemical analysis between the quantities of the components a and b is the same in the solid $A_x B_y$ [left hand side of equation 5*a*] as in the solution [right hand].

(Note :—Each molecule of A counts for *m* molecules of a in the (chemical analysis); the presence of molecules $A_x B_y$ in the solution does not affect the result and is not indicated in equation 5*a*).

W. L. M.

A Study of Liquefied Gases. *P. Villard. Ann. chim. phys.* (*7*) **10**, *387* (*1897*). The gases used (N_2O, CO_2, C_2H_4, C_2H_2) were purified by boiling off volatile impurities. Tables are given of the vapor pressures for various temperatures between − 140° and + 20°. The pressures were read on a metallic gauge which had been calibrated. The second and larger part of the paper contains a very interesting study of the phenomena observed near the critical point. The author discusses the various hypotheses regarding the state of the substance and concludes that the simple assumption of total evaporation and a unique density is sufficient when account is taken of gravity and the variability of temperature along the tube. For the details we must refer to the original. *E. B.*

Contributions to the Knowledge of the Favorable Conditions for the Crystallization of Carbon. *W. Borchers. Zeit. Elektrochemie*, **3**, *393* (*1897*). The author states that all substances which form alloys or easily decomposable compounds with carbon increase its tendency to crystallize. He therefore suggests that if a fraction of a percent of any of these substances be added to a mass of carbon and the latter heated electrically it might possibly change into large diamonds. *W. D. B.*

On the Effect of Pressure, *etc. Wilson and Fitzgerald. Roy. Soc. Proc.* **60,** *377* (*1897*). Reviewed in this Journal **1,** 438; from Astrophys. Jour. **5,** 101 (1897).

On Some Earlier Determinations of the Freezing-points of Saturated Salt Solutions. *L. C. de Coppet. Zeit. phys. Chem.* **22,** *239* (*1897*). The author republishes from the Bulletin de la Société Vaudoise des Sciences naturelles (2) **11,** 1 (1871) some determinations of the cryohydric temperatures and concentrations of fifteen salts. *W. D. B.*

Methyl Oxalate in Cryoscopy. *G. Ampola and C. Rimatori. Rend. Accad. Lincei,* (*5*) **5,** *404* (*1896*). Thirteen substances out of thirteen gave unsatisfactory results with methyl oxalate as solvent. Since the molecular depression varies greatly with the concentration, it is possible by taking entirely different concentrations of the different solutes to get the same molecular depression. In this arbitrary way the authors obtain *52.87* as the constant for methyl oxalate. In this constant there are no significant figures. *W. D. B.*

On the Ammonia Compounds of Silver Chlorid. *R. Jarry. Comptes rendus,* **124,** *288* (*1897*). Working with an ammoniacal solution of silver chlorid at 0° the author found the pressure remaining constant at *268* mm and again at *17* mm. The dissociation pressures of the dry compounds $AgCl_3NH_3$ and $2AgCl_3NH_3$ are respectively *262* mm and *12* mm at 0°. Though there is nothing in the paper to show it, the measurements in presence of water were undoubtedly made upon saturated solutions. The author determined the solubility of silver chlorid in ammonical solutions without making any reference to Bodländer's work. *W. D. B.*

Some Double Haloids of Magnesium with Potassium and Ammonium. *A. de Schulten. Bull. soc. chim. Paris,* **17,** *165, 167, 169* (*1897*). The author has made the salts $NH_4ClMgCl_2,6H_2O$, $KBrMgBr_2,6H_2O$, and $NH_4BrMgBr_2,6H_2O$. He states that no double haloids of magnesium and sodium can exist. *W. D. B.*

Double Haloids of Lead and Ammonium. *H. Fonzes-Diacon. Bull. soc. chim. Paris,* **17,** *346* (*1897*). The author has analyzed a large number of double salts, some being with mixed haloids. None of the systems examined were studied in detail. *W. D. B.*

On Certain Abnormal Instances of Solubility. *H. Le Chatelier. Zeit. phys. Chem.* **22**, *250 (1897)*. Reprinted from the Comptes rendus, **123**, 746 (1896) and reviewed in this Journal **1**, 259 (1897). *W. D. B.*

The Freezing-point of Dilute Aqueous Solutions. III. *E. H. Loomis. Wied. Ann.* **60**, *523 (1897)*. Reviewed in this Journal **1**, 312; from Phys. Rev. **4**, 273 (1896).

Divariant Systems

On the Principle of Avogadro-Ampère Considered as a Limiting Law. *A. Leduc. Comptes rendus, 124, 285 (1897)*. An attempt to verify the author's previous proposition that *at corresponding temperatures and pressures all gases have the same molecular volume* which he regards as more general than the law of corresponding states. The failure to define molecular weight makes it impossible for the reviewer to criticise the paper. The author appears satisfied with the experimental confirmation of his proposition. *E. B.*

Verification of the Law of Corresponding States of van der Waals; Determination of Critical Constants. *E. H. Amagat. Jour. de Phys. (3)* **6**, *5 (1897)*. See this Journal, **1**, 66. The author gives a very neat method of testing the law without reference to any empirical formulas. To compare two substances photograph their isotherm-nets. Place the negatives on an optical bench with a long-focus lens between them. Project one on the other by the lens, changing the scales if necessary by tipping one of the plates about vertical and horizontal axes. If the two nets can, by this means, be made to coincide, the law of corresponding states holds for those two substances and, as the author shows, the critical data of one may be found from those of the other. The method is tested for CO_2, C_2H_4, ether and air. The agreement of the projected nets (which is shown by figures on an enlarged scale) is within the limits of error of observation, so that for these substances the law holds within the range of the diagrams. *E. B.*

On the Densities of Nitrogen, Oxygen and Argon and on the Composition of Atmospheric Air. *A. Leduc. Comptes rendus*, **123**, *805* (*1896*). Determinations as follows:—

	Oxygen	*Nitrogen*	*Argon*
Density	1.10523	0.9671	1.376
Weight of a liter	1.4293 g.	1.2507 g.	1.780 g.

Composition of air:—

a. By weight	75.5	23.2	1.3
b. By volume	78.06	21.0	0.94

J. E. T.

The Spontaneous Change of Oxygen into Ozone and a Remarkable Type of Dissociation. *W. Sutherland. Phil. Mag.* [*5*] **43**, *201* (*1897*). Bohr found that oxygen did not follow the law of Boyle when the pressure falls below *0.7* mm. From this the author concludes that if the external pressure be decreased sufficiently oxygen will condense spontaneously to ozone. Comment seems to be superfluous. *W. D. B.*

Description of a Simple Apparatus for Determining the Molecular Weight of Substances in Dilute Solutions. *G. Guglielmo. Rend. Accad. Lincei,* (*5*) **5**, *395* (*1896*). By means of a U-tube terminating at one end in a bulb and a capillary which can be closed, the author determines the decrease in vapor pressure due to the presence of the solute at the boiling point of the pure solvent. The method involves the knowledge of the density of the solution. It gives very good results in the hands of the author but is not likely to come into general use. *W. D. B.*

On the Determination of Rise of Boiling Temperature for the Purposes of Molecular Weight Determinations. *Paul Fuchs. Zeit. phys. Chem.* **22**, *72* (*1897*). A description of another complicated apparatus for determining the boiling temperatures of solutions. The only point worthy of notice is the avoidance of cork or rubber seals,—mercury being used.

It is somewhat amusing to read of such complicated arrangements, for an apparatus essentially the same as that of Orndorff and Cameron, Am. Chem. Jour. **17**, 517 (1895), has given complete satisfaction to the reviewer and that too at pressures ranging from 50 mm to 760 mm. It was far more accurate than that of Fuchs. *C. L. S.*

On the Volatilization of Lactic Acid and its Anhydrids at ordinary Temperatures and on the Distillation of Lactic Acid with Water Vapor. *J. A. Muller. Bull. soc. chim. Paris*, **15**, *1206* (*1896*). Lactic acid and lactid volatilize in measurable quantities on standing over solid potassium hydroxid. When a solution of lactic acid is distilled the amount of acid in the distillate varies proportionally to the acid in the distilling flask. *W. D. B.*

On the Absorption of Hydrogen Gas by Platinum at Different Temperatures. *L. Anelli. Nuovo Cimento*, (*4*) **4**, *257* (*1896*). The author's results agree fairly well with those of Graham, the only measurements of which he seems to have heard. *W. D. B.*

Polyvariant Systems

The Oxidation of Nitrogen Gas. *Lord Rayleigh. Jour. Chem. Soc.* **71**, *181* (*1897*). Davy's statement that nitrogen is oxidized during electrolysis is not correct. The author has studied the oxidation of nitrogen gas under the influence of the electric discharge. Increased size of vessel increases the rate of oxidation while increased pressure has only a slight accelerating influence. The author uses a fountain of alkali in order to ensure rapid absorption of the oxidation products. *W. D. B.*

Diffusion of Solids into Gases. *A. Colson. Bull. soc. chim. Paris* **17**, *164* (*1897*). The author recalls that in 1881 he showed that if cold sulfurous acid be passed over lead dioxid a precipitate of lead sulfate will be formed on the walls of the tube, indicating that this substance is volatile in sulfurous acid. *W. D. B.*

The Direct Union of Carbon and Hydrogen. *W. A. Bone and D. S. Jerdan. Jour. Chem. Soc.* **71**, *41* (*1897*). At about 1200°

carbon unites with hydrogen to form methane and methane only. At the temperature of the electric arc there is equilibrium between hydrogen, methane and acetylene. The authors propose to study this equilibrium more in detail. *W. D. B.*

On a New Method of Preparing Alloys. *H. Moissan. Bull. soc. chim. Paris.* **15**, *1282* (*1896*). If an oxid of any of the refractory metals be poured into melted aluminum there is formed an aluminum alloy of that metal. *W. D. B.*

Effect of Heat on Aqueous Solutions of Chrome Alum. *M. D. Dougal. Jour. Chem. Soc.* **69**, *1526* (*1897*). The green solution is less dense than the violet solution. From diffusion experiments it was found that the green diffusate contains less chromium and more sulfuric acid than the violet diffusate. These results are in harmony with the conclusions of Monti and of Whitney that the green solution contains chromosulfuric acid. *W. D. B.*

Decomposition of Mercuric Sulfate by Water. *Guinchant. Bull. soc. chim. Paris*, **15**, *1185* (*1896*). A polemic against Varet because the latter assumes the existence in solution of acid instead of neutral mercuric sulfate. *W. D. B.*

On Organic Compounds which prevent the Formation of the Insoluble Hydroxids of Iron, Nickel and Copper. *J. Roszkowski. Zeit. anorg. Chem.* **14**, *1* (*1897*). The author gives a list of the organic compounds known to form complex salts with iron, nickel and copper, together with an account of the behavior of aqueous and of alcoholic potash when the salt or the organic substance is present in excess. *W. D. B.*

The Formation of ‹Active› Oxygen in the Slow Oxidation of Triethyl Phosphine, etc. *W. P. Jorissen. Zeit. phys. Chem.* **22**, *34* (*1897*). The formation of ozone by the slow oxidation of phosphorus in moist air has long been observed; quantitative experiments on the subject however were first carried out by van 't Hoff, Zeit. phys. Chem. **16**, 311 (1895), who found that, for every thirty-one grams of phosphorus oxidized, about eight grams of oxygen were converted into ozone, or at all events rendered ‹active› enough to oxidize a solution of indigo sulphonate of sodium.

As under the conditions of the experiment a mixture of several oxidation products of phosphorus was formed, the study of simpler cases seemed desirable; these Jorissen has found in the oxidation of trethyl phosphine (to triethyl phosphine oxid) and of benzaldehyde (to benzoic acid) by air in the presence of water.

Weighed quantities of the phosphine (or aldehyde) were mixed with a known volume of a titrated solution of sodium indigo sulphonate in a closed vessel provided with a manometer; the total amount of oxygen absorbed was calculated from the diminution in pressure and a subsequent titration showed that in every case close on half of this amount was absorbed by the indigo solution; in other words, the phosphine (or aldehyde) on slow oxidation renders ‹active› almost exactly as much oxygen as it itself absorbs. Warmth and light accelerate the reaction without altering the results.

Propionic aldehyde seems to act in much the same way, and a review of the experiments of others on the oxidation of lead amalgam and of zinc amalgam and on the solution of gold in potassium cyanid shows that in these cases also the ‹active› oxygen formed is roughly equal in amount to that absorbed by the oxidation of the substances in question. *W. L. M.*

The Formation of Benzoyl- and Propionyl-peroxids by ‹Active› Oxygen. *W. P. Jorissen. Zeit. phys. Chem.* **22**, *54* *(1897)*. In a glass apparatus provided with a manometer, weighed quantities of benzaldehyde and of acetic anhydride were subjected to the action of oxygen. The rate of the reaction is much accelerated by light and by the addition of a little coarse sand to increase the surface of the liquids. The amount of oxygen absorbed, as obtained from readings of the manometer, was in every case very nearly twice that necessary to convert all the aldehyde present into benzoic acid. When the pressure became constant the contents of the apparatus were examined and benzoyl peroxid found to be present. In the absence of acetic anhydrid on the other hand, only enough oxygen is absorbed to convert the aldehyde into benzoic acid. Experiments with propionic aldehyde instead of benzaldehyde gave similar results.

The author seeks to represent the reactions involved by means of the following equations :—

$C_6H_5CHO + O_2 = C_6H_5COOH + O$ *active.*
$(CH_3CO)_2O + O$ *active* $= (CH_3CO)_2O_2$
$(CH_3CO)_2O_2 + 2C_6H_5COOH = (C_6H_5CO)_2O_2 + 2CH_3COOH$

These equations however only account for the absorbtion of *one* atom of ‹active› oxygen for every *two* molecules of benzaldehyde oxidized. Does the product of oxidation perhaps contain acetyl peroxid as well as benzoyl peroxid? *W. L. M.*

On the Change of Volume in the Formation of Solutions. *G. Tammann. Zeit. phys. Chem.* **21**, *529* (*1896*). Let v' = volume of solution containing 1 gram molecule of solute, v'' = volume of solvent, φ = so-called molecular volume of solute; then $\varphi = v' - v''$. Let Φ = volume of the body to be dissolved, $\Delta\Phi$ = change of Φ when the dissolving body passes from its own internal pressure to the pressure in the solution, $\Delta v''$ = change of volume of the solution when the interval pressure changes from that of the solvent to that of the solution, $\Delta\Sigma v$ = change of volume on dissolving under the internal pressure of the solvent; then $\varphi = \Phi + \Delta\Phi + \Delta v'' + \Delta\Sigma v$. The observable change of volume Δv on dissolving is $\Delta v = \varphi - \Phi = \Delta\Phi + \Delta v'' + \Delta\Sigma v$. The paper consists of speculations of no particular value at present, on these quantities together with a few experimental data. It closes with a warning to experimenters on molecular volumes. [The excellent results of Traube, Ber. chem. Ges. Berlin, 1894 and *ff* are not mentioned. R.] *C. L. S.*

The Determination of the Freezing-point of Milk as a Means of discovering and estimating the Adulteration with Water. *H. J. Hamburger. Recueil Trav. Pays-Bas*, **15**, *349* (*1896*). The author finds that milk from different cows has about the same freezing-point, the mean depression being *0.561°*. Curiously enough the author seems to be ignorant of the fact that this same result was obtained by Winter long ago and has been the subject of much discussion in the Comptes rendus ever since. *W. D. B.*

Osmotic Pressure

Direct Measurement of Osmotic Pressure. *A. Naccari. Rend. Accad. Lincei*, (*5*) **6**, *32*; *Nuovo Cimento*, (*4*) **5**, *141* (*1897*). Using

Pfeffer's method and four percent solutions the author has obtained measurements with glucose, salicin and mannit which agree marvelously with the theoretical values. With antipyrin the experimental values are three percent high, a variation which the author considers unaccountable; but which most people would consider too small to mention. It was noticed that three out of four copper ferrocyanid membranes were somewhat permeable to glycerol even when all four were impermeable to sugar; in other words there are marked differences in the properties of the coherent films even when made of the same substance in the same way. The author also noted that even with pure water an osmotic pressure is obtained. The reason for this was not made out; but it seems reasonable to suppose that salts in the membrane may have had something to do with it. *W. D. B.*

On the Diffusion of Sulphides through Steel. *E. D. Campbell. Am. Chem. Jour.* **18**, *107* (*1896*). Iron oxysulfid diffuses through steel but iron sulfid and subsulfid do not. Copper sulfid does not diffuse by itself but does in presence of iron oxysulfid. Nickel sulfid does not diffuse even in presence of iron oxysulfid.

W. D. B.

Chemical Action at a Distance. *R. E. Liesegang. Separate reprint, Düsseldorf,* (*1896*). A series of interesting diffusion experiments with sodium chlorid and silver nitrate in gelatin. The assumption of chemical action at a distance is uncalled for.

W. D. B.

Velocities

The Hydrolysis of Acid Amides. *I. Remsen. Am. Chem. Jour.* **19**, *319* (*1897*). A note to the effect that studies on the rate of change of nitrobenzamids into the ammonium salts in presence of acids have shown that the para-compounds are the most readily attacked and the ortho-compounds the least readily. *W. D. B.*

On the Volatility of Certain Inorganic Salts. *T. H. Norton and D. M. Roth. Jour. Am. Chem. Soc.* **19**, *155* (*1897*). The authors have determined the time necessary to volatilize 0.01 g of different salts when introduced as a bead on a platinum wire into the hottest part of a Bunsen flame. The salts taken were the sulfates, carbonates, chlorids and fluorids of sodium and potassium, the bromid and iodid of potassium, sodium borate, barium chlorid and lithium chlorid. The values vary very perceptibly from those obtained by Bunsen. *W. D. B.*

Facts bearing upon the History of Metaphosphoric Acid. *M. Berthelot and G. André. Comptes rendus.* **124**, *265 (1897).* Sodium metaphosphate which has been obtained by ignition changes into pyrophosphate and orthophosphate in solution much more slowly than sodium metaphosphate which has only been heated to 280°. *W. D. B.*

Action of Melted Sodium Hydroxid under Pressure on Cast and Wrought Iron. *Scheurer-Kestner. Bull. soc. chim. Paris.* **15**, *1850 (1896).* Owing to an accident occurring in a French factory it was discovered that fused sodium hydroxid attacks wrought iron fairly readily, cast iron to a lesser extent. *W. D. B.*

Action of Hydrochloric Acid in Different Solvents upon Zinc. *F. Zecchini. Rend. Accad. Lincei. (5)* **6**, *149 (1897).* For the same volume concentration of acid, zinc is dissolved at rates varying with the solvent. The order is: ether, acetone, methyl alcohol, ethyl alcohol, water and amyl alcohol, the action being greatest in ether and least in amyl alcohol. Addition of small quantities of water to ether increases the reaction velocity; but addition of water to acetone, methyl or ethyl alcohol decreases it. These results are quite unexpected and very interesting. The author suggests that the volatility of the solvent may affect the rate of attack. It would seem more profitable to consider the question of the volatility of the acid and perhaps also the question of the solubility of the zinc chlorid. *W. D. B.*

The Explosion of Acetylene with less than its own Volume of Oxygen. *W. A. Bone and J. C. Cain. Jour. Chem. Soc.* **71**, *26 (1897).* The products of the explosion are carbon monoxid, hydrogen, carbon and traces of carbon dioxid. The excess of acetylene is converted almost entirely into its components by the shock and no methane is formed. *W. D. B.*

Note. *G. W. Rolfe and G. Defren. Jour. Am. Chem. Soc.* **19,** *261 (1897).* A long list of errors and misprints in a paper reviewed in this Journal **1,** 382.
J. E. T.

Theoretical Considerations Respecting the Separation of Gases by Diffusion and Similar Processes. *Lord Rayleigh. Phil. Mag. [5]* **42,** *493 (1896).* A series of calculations regarding the concentration of argon from the atmosphere by the method of atmolysis. The gases are first supposed to diffuse into a vacuum, and only the residue is considered. Let x, y, be the quantities of the two constituents of the residue at any time, $-dx$, $-dy$, are the quantities diffused out in time dt. Hence $dx/dt = \nu y/\mu x$, (1), where μ and ν are the diffusion rates. Integrating, $y^{1/\nu} = Cx^{1/\mu}$, (2), or $y/x = Cx^{-1+\nu/\mu}$, (3), where C is a constant. If X, Y, be simultaneous values of x, y, regarded as initial, $(y/x)/(X/Y) = (x/X)^{-1+\nu/\mu}$, (4), so that $x = X[(y/x)/(Y/X)]^{\mu/(\nu-\mu)}$, (5). Similarly, $y = Y[(x/y)/(X/Y)]^{\nu/(\mu-\nu)}$, (6). Putting $(y/x)/(Y/X) = r$, (7), so that r represents the enrichment of the residue as regards the second constituent, we have from (5) and (6), $(x+y)/(X+Y) = [X/(X+Y)]r^{\mu/(\nu-\mu)} + [Y/(X+Y)r^{\nu/(\nu-\mu)}$, (8). From (4) it is evident that as x diminishes with t, the enrichment tends towards 0 or ∞, indicating that the residue becomes purer without limit. The results of Graham's experiments and the calculations with the above equations do not agree. The author thinks this difference is due to imperfections in the walls and joints of Graham's apparatus. When the vacuum is replaced by an atmosphere of fixed composition, suppose that only two gases are concerned and that the volume inside is given. Let x, y, denote the partial pressures within the given volume, the constant partial pressures outside being α; β. We have $dx = \mu(\alpha - x)dt$, $dy = \nu(\beta - y)dt$, (9), or on integration, $x = \alpha + Ce^{-\mu t}$, $y = \beta + De^{-\nu t}$, (10) where C and D are arbitrary constants. The constants μ and ν are not known beforehand, depending upon the apparatus and quality of the gases. Eliminating t we get $y - \beta = E(x - \alpha)^{\nu/\mu}$, (11) in which only the ratio of μ and ν appears.

When the gases diffuse into a vacuum suppose the $(\nu - \mu)/\mu = \kappa$ is a small quantity. At each operation, one-half the total volume of the mixture is allowed to pass. Then (8) becomes $1/2 = [X/(X + Y)]r^{1/\kappa}$

$+[Y/(X+Y)]r^{(1+\kappa)/\kappa}=r^{1/\kappa}$ nearly, so that $r=(y/Y)/(x/X)=(1/2)^\kappa$, (15). If s corresponds to r for the transmitted gas,

$$s=\frac{(Y-y)/Y}{(X+x)/X}=\frac{1-y/Y}{1-x/X}=\frac{1-rx/X}{1-x/X}$$

$$=1+\frac{(1-r)x/X}{1-x\ /X}=2-r,$$

approximately, since r nearly $=1$. Accordingly,

$$1/s=1/(2-r)=r, \text{ nearly.}$$

Approximately then, s and r are reciprocal operations. That is, starting with any proportions, collecting the transmitted half, submitting it to another operation, retaining the half not transmitted, the final composition corresponding to the operations sr is the same (approximately) as the composition with which we started, and the same also as would be obtained by operations taken in the reverse order rs. The result of n sets of operations is $[(r+s)/2]^n$. When the transmitted gas is not one-half but a fraction σ, and ρ is the fraction of the retained gas, such that $\rho+\sigma=1$, we have, instead of (15), $r=\rho^\kappa$, and $\rho r+\sigma s=1$, and the various portions into which the gas is divided after n sets of operations are represented by the various terms of the expansion $(\rho r+\sigma s)^n$, the Greek letters and the numerical coefficients giving the quantity of each portion, and the Roman letters giving the quality. *C. L. S.*

Electromotive Forces

On the Displacement of Phase caused by the Action of Alternating Currents on a Voltameter. *R. Malagoli. Nuovo Cimento,* (*4*) 4, *296* (*1896*); 5, *29* (*1897*). After a discussion of the results of Peukert and the theoretical views of v. Dolivo-Dobrowolsky the author deduces the following conclusions for a voltameter and a sinusoidal electromotive force:

I. The polarization which is perpendicular to the current is in advance of the fundamental electromotive force, the amount increasing with decreasing frequency, resistance and capacity of the voltameter.

II. With increasing displacement there is an increase in the maximum polarization and a decrease in the intensity.

III. The effective potential difference at the electrodes is as much behind the fundamental electromotive force as behind the current, and the lag with respect to the latter decreases with increasing resistance in the voltameter.

In the second paper the author tests his views experimentally for the cases where there is and is not visible electrolysis, getting very satisfactory results. *W. D. B.*

On an Absolute Electrometer for the Measurement of Small Differences of Potential. *A. Pérot and C. Fabry. Comptes rendus,* **124**, *180* (*1897*). The improvement consists in two plane silvered glass plates only one-tenth of a millimeter apart. *W. D. B.*

On a New Accumulator. *D. Tommasi. Bull. soc. chim. Paris,* **17**, *211* (*1897*). The electrodes consist of a lattice work of an alloy of antimony and lead placed in a perforated celluloid case, the intervening spaces being filled with the lead dioxid. Since the lattice work does not have to support the active mass, it can be made very much lighter than is usual. The accumulator is said to give 12-15 amperes per kilogram of electrode if necessary. *W. D. B.*

On Professor Hermann's Theory of the Capillary Electrometer. *G. J. Burch. Roy. Soc. Proc.* **60**, *329* (*1896.*) According to the author's theory of the time relations of the capillary electrometer, there are several links between the electrical cause and the mechanical effect, and a strong probability that each of them involves a time function. These are: (*a*) A difference of potential (the establishment of which is delayed by the varying internal ohmic resistance of the electrometer), this produces (*b*) a change in the constant of capillarity at two interfaces between mercury and an electrolyte, presumably giving rise to (*c*) polarization at the aforesaid interfaces; and (*d*) does work in moving a column of mercury against the force of gravity with more or less rapidity according to the varying amount of fluid friction in the tube. Of these Hermann, Arch. f. d. ges. Physiologie, **63**, 440, has neglected (*b*) and (*d*), confining himself to the theoretical relations between (*a*) and (*c*).

«The locus of transformation from electrical to mechanical force must clearly be the two interfaces mercury-acid and acid-mercury, and it is upon these that the stress acts. The resistance is distributed along the tube, and is partly electrical, but to a far greater extent mechanical. It is reasonable, therefore, to assume that the sole cause of delay is the *Polarisations-Geschwindigkeit* of the meniscus?» *W. L. M.*

Electromotive Force; a reply to Dr. A. H. Bucherer. *R. Luther. Zeit. phys. Chem.* **22**, *85* (*1897*). As to priority, the author's article was handed in as dissertation a month before Bucherer's article, Elektrochem. Zeit. **2**, 217, appeared. The author points out that a theory which, like Bucherer's, takes for granted the gas laws, Faraday's law, and van 't Hoff's laws for solutions, *etc.*, can hardly lay claim to the title of a «purely ‹energetic› theory»; replies to several of Bucherer's criticisms of the ‹Planck-Nernst-Ostwald› electrochemical theory, this Journal **1**, 130, and, after a résumé of the theory in question, concludes as follows: «From a theoretical point of view it is perfectly possible to calculate the E.M.F. of galvanic elements from the vapor tensions of the reacting substances, and the calculation if properly carried out will lead to correct results; the classical researches of Helmholtz and van 't Hoff have long ago shown how numerical results may be obtained in this manner. In general however, our ignorance of the vapor tensions of the metals, *etc.*, renders the attainment of quantitative results by this method impracticable; and the great advance brought about by van 't Hoff's introduction of the conception of osmotic pressure is due to the fact that in place of vapor tensions, for the most part unknown, the easily ascertainable concentrations of the substances in solution are made the basis of the calculation. To desert this standpoint would be to give up all attempts at a quantitative description of the phenomena in question».

In one point however it appears to the reviewer that Bucherer is quite right, *viz*:—where he insists on the difference between cells involving saturated solutions of hydrated salts and those in which the salts crystallize without water.

In a Clark's cell the change brought about by the passage of a current may be represented by the equation

$$\mathrm{Zn} + \mathrm{Hg_2SO_4}\ \textit{solid} + 7\mathrm{H_2O}\ \textit{from the solution} \rightleftarrows 2\mathrm{Hg} + \mathrm{ZnSO_4 7H_2O}\ \textit{solid}.$$

Addition of alcohol, salts, *etc.*, can hardly fail to alter the tension of the aqueous vapor given off by the electrolyte, *i. e.* the chemical potential of the water, and consequently the E.M.F. of the cell. Measurements of the E.M.F. of cells of this type (to which varying quantities of alcohol, for example, have been added) might indeed prove the means of quantitatively determining alterations in the vapor tension in question. *W. L. M.*

The Employment of Cyanids in Galvanic Cells and in Accumulators. *G. Platner. Elektrochem. Zeit.* **3**, *265* (*1897*). The author proposes to use potassium ferricyanid as electrolyte with Turnbull's blue or potassium chlorate as depolarizor. It is not clear from the paper what the cathode is to be, nor how the cell is arranged; but we are assured that the electromotive force will be *1.6 v.* *W. D. B.*

On the Iron, Ferric Chlorid, Carbon Cell. *F. W. Küster. Zeit. Elektrochemie*, **3**, *383*, (*1897*). The author disputes the view of Pauling that ferric chlorid is formed at the anode and shows that iron dissolves in ferric chlorid solution on open circuit with formation of ferrous chlorid. Pauling's cell is therefore worthless. *W. D. B.*

The Lead Cell. *B. E. Moore. Phys. Rev.* 4, *353* (*1897*). This is nominally an attempt to formulate a theory of the lead accumulator. Practically it consists of the statement that on closed circuit there will be a tendency to form concentration differences at the two electrodes thus causing a change in the electromotive force in the first few minutes after closing the circuit. He shows this to be true experimentally. The author does not seem to be familiar with the literature of his subject since he complains that the temperature coefficient of the accumulator is not known, entirely overlooking the measurements of Streintz, Wied. Ann. **49**, 568 (1893). *W. D. B.*

Discussion. *Bucherer, Nernst, Neuburger. Elektrochem. Zeit.* **3**, *235*, *284* (*1897*). Bucherer wished to answer a review of some of his work which had appeared in the Zeit. Elektrochemie; but publication was refused by Nernst unless a passage criticizing certain views of Nernst was omitted. The letter was published in the Elektrochem. Zeit. and Nernst justified his action on the ground that the criticism was not valid. Incidentally he makes some unpleasant and uncalled for remarks about the elektrochem. Zeit. for which he is promptly scored by Neuburger. The tone of all three disputants is about as bad as it can be. *W. D. B.*

Electricity from Carbon without Heat. *W. E. Case. Electrical Engineer,* **23**, *244* (*1897*). A lecture delivered before the New York Electrical Society in which the speaker put forward the remarkable hypothesis that the oxidation of carbon by chloric acid might readily be expected to give the same electromotive force as the oxidation of carbon by oxygen. *W. D. B.*

On the Influence of the Röntgen Rays upon the Explosive Distance of the Electric Spark. *Guggenheimer. Comptes rendus* **124**, *359* (*1897*). The author finds that under constant potential difference the spark will jump farther when exposed to the Röntgen rays than when in the dark. This is analogous to the results obtained by Hertz with ultra-violet rays and is probably due to a change in the dielectric. *W. D. B.*

On Some Experiments with Röntgen's Rays. *R. Threlfall and J. A. Pollock. Phys. Soc. Lond. Proc.* **15**, *1* (*1897*). Those conclusions of the authors, which have physicochemical interest, are that a very pure selenium cell with platinum electrodes is affected by Röntgen radiation to much the same extent as by diffused daylight; and that no permanent or temporary E. M. F. is set up in such a cell by the radiation. *J. E. T.*

Electric Potentials in a Moving Liquid. *G. G. de Villemontée. Jour. de Phys.* (*3*) **6**, *59* (*1897*). Electrodes are placed at various points in a glass tube drawn out to a fine point at one end. When Hg is run through the tube no E.M.F. could be observed between the electrodes, the position of the electrodes, the diameter of the tube and the velocity of flow being widely varied. One of the electrodes was also tried in the issuing jet. Similar experiments with dilute $CuSO_4$ and $ZnSO_4$ also gave no E.M.F. With distilled water (a badly conducting liquid) experiment showed an E.M.F. between the jet and the liquid in the tube or between two points in the tube. For tubes satisfying the law of Poiseuille the E.M.F. between reservoir and jet is, for a given pressure, independent of the length and cross section of the tube. For larger tubes no general law can be given. For the details of the author's conclusions we must refer to the original paper. *E. B.*

On the Theory of Thermoelectricity. *R. Mewes. Elektrochem. Zeit.* **3**, *263* (*1897*). An effort to account for the phenomena of thermocurrents, from the laws of «heat conduction frequency». *J. E. T.*

Electrolysis and Electrolytic Dissociation

On the Specific Gravity and Electrical Conductivity, *etc. E. H. Loomis. Wied. Ann.* **60**, *547* (*1897*). Reviewed in this Journal **1**, 324; from Phys. Rev. **4**, 252 (1897).

On the Calculation of the Conductivity of Electrolytes. *J. G. MacGregor. Trans. Roy. Soc. Canada* (*2*) **2**, *65*, (*1896*). The author discusses the conditions for equilibrium in solutions containing two electrolytes with a common ion; any number of electrolytes having a common ion; two electrolytes having no common ion; three electrolytes having no common ion; any number of electrolytes with no common ion; any number of electrolytes with no common ion, the products of their double decomposition and any other electrolytes. The only fault to be found with this is that the author assumes the validity of Ostwald's dilution law which does not apply experimentally to salts. Until we can express the change in dissociation of a single electrolyte by a rational formula, the study of solutions containing any number of electrolytes is merely practice in handling mathematical equations. *W. D. B.*

On the Molecular Conductivity of Salts in Dilute Solutions. *P. Joubin. Comptes rendus,* **124**, *228* (*1897*). A feeling for symmetry rather than for facts causes the author to accept Bouty's hypothesis that the molecular conductivity of all salts is the same for infinite dilution. *W. D. B.*

Remarks relative to a Note on the Oxidation of Sodium Sulfid during Electrolysis. *Scheurer-Kestner. Bull. soc. chim. Paris.* **17**, *99* (*1897*). The author made some experiments in 1881 showing that sodium sulfid is oxidized directly to sulfate and that neither sulfur nor thiosulfate is formed. This contradicts the results of Durkee, Am. Chem. Jour. **18**, 525 (*1896*). *W. D. B.*

On the Electrolysis of Copper Sulfate Solutions. *F. Foerster and O. Seidel. Zeit. anorg. Chem.* **14**, *106* (*1897*). An extended and very interesting series of investigations. The authors find that under suitable conditions cuprous sulfate is formed during the electrolysis with cuprous oxid precipitated in consequence. If a hot acidified solution of copper sulfate be electrolyzed and then allowed to cool, the presence of cuprous sulfate in the solution is shown by the formation of metallic copper all through the liquid. For the bearing of the results upon the copper voltameter and upon the theory of the lead accumulator, the reader is referred to the article itself. *W. D. B.*

Reactions of Carbon on Electrolysis. *F. Vogel. Zeit. angew. Chem.* **1897**, *18*. A lecture delivered in Berlin. It was pointed out that in all cases in which carbon is anode and is attacked, organic products are formed and that it is therefore improbable that carbon has ever burned to carbonic acid in a galvanic cell. *W. D. B.*

The Molecular Conductivities of Caesium and Rubidium Chlorides. *B. B. Boltwood. Zeit. phys. Chem.* **22**, *132* (*1897*). Large quantities of the salts were prepared and purified. The measurements give:

μ_∞ for	KCl	141.5	hence u for	K	71.3
	RbCl	144.5		Rb	74.3
	CsCl	144.8		Cs	74.6

W. L. M.

Contributions to the Constitution of Salt Solutions. *H. Ley. Zeit. phys. Chem.* **22**, *77* (*1897*). When a blue aqueous solution of $CuCl_2$ is heated, it turns green. The stronger the solution, the lower the temperature at which the change occurs. The author thought this might be due to a re-formation of $CuCl_2$ from its ions as the temperature rose. A determination of electric conductivity however did not support this view; there were no singular points in the curve relating temperature and conductivity. The author thinks this may be due to a balance between $CuCl_2$ and its ions according to the two equations $CuCl_2 = Cu^{++} + 2Cl^-$ and $CuCl_2 = CuCl^+ + Cl^-$. Experiments were also made with absolute alcohol, acetone, and pyridin as solvents. The pyridin solution was blue, but did not seem to contain appreciable quantities of ions, for its conductivity was extremely small, $v = 30$, $\lambda = 0.05$. *C. L. S.*

On the So-called Autoxidation. *R. Ihle. Zeit. phys. Chem.* **22**, *114* (*1897*). Autoxidation is the oxidation which metals like iron, zinc and aluminum rapidly undergo in aerated water. They retain their lustre much longer in aerated water rendered slightly alkaline with NaOH. Carbonates, phosphates, borates, nitrites, of the alkalies act like NaOH; soluble chlorids, bromids, iodids, chlorates, nitrates, sulfates, and probably all neutral salts, increase the autoxidation. The author tries to explain these facts by the ionic theory, but the explanation is not very clear.

The other part of the paper is much clearer. Hydrogen peroxid can give H^+ or OH^- according to conditions, H^+ being produced with bodies which give O_2^{--} or a similar ion, and OH^- being produced with bodies which give H^+ or a similar ion. Bright potassium in an acidified solution of H_2O_2 has a potential difference of 1.078 volt, in an alkaline solution of H_2O_2 it has a potential difference of 0.367 volt. AgBr in KBr has potential difference of 0.42 volt, so ionic tension of anion in the latter case is greater than ionic tension of OH^- in H_2O_2 in alkaline solution. So Br^- passes off from AgBr in alkaline H_2O_2 solution, so this solution reduces AgBr and may be used as a photographic developer. In acid solution of H_2O_2, AgBr is not changed. In acid solution, K_3FeCy_6 has potential difference of 1.021 volt; in alkaline solution it has a potential difference of 0.886 volt. So in acid solution, reaction with H_2O_2 should be slight, in alkaline solution however, ionic tension of anion is greater than that of OH^- in H_2O_2 and so K_3FeCy_6 should pass into K_4FeCy_6, which it does. *C. L. S.*

On the Change of the Coefficient of Refraction in the Neutralization, Formation and Dilution, of Solutions. *G. Tammann.*

Zeit. phys. Chem. **21**, *537*, (*1896*). Let n = coefficient of refraction; then at low pressures, according to Quincke, $(n - 1)/d$ is constant for a number of liquids. Replacing d by $1/v$ and differentiating according to the external pressure $p_1[d(n - 1)]/dp = -(n - 1)(1/v)dv/dp$ (1). The paper consists of speculations and applications of this equation, from which the author concludes that :—

«The formula of Quincke for the dependence of n on the external pressure seems to be also true for considerable variations in the internal and external pressure of water. Electrolytic dissociation hardly changes n; bodies containing H and OH are exceptions. The equivalent refraction of hydrogen increases on ionization 1.8 units and that of hydroxyl 0.7 units. On changing from NH_3 and the hydrogen ion into ammonium, the equivalent refraction increases 3.2 units.» *C. L. S.*

The Effect of the Solvent on the Migration Velocity of the Ions. *C. Cattaneo. Rend. Accad. Lincei* (*5*) **5**, *207* (*1896*). The transference numbers for NaCl and NH_4Cl are found to be about the same whether glycerol or water be solvent though the conductivity is much less in the glycerol solutions. *W. D. B.*

On the Sensitiveness of Indicators. *E. Lunge and E. Marmier. Zeit angew. Chem.* **1897**, *3*. The authors find that methyl orange is more sensitive than dimethylanilinazobenzene at ordinary temperatures. At 40° both are useless as indicators. The color reactions of the two substances are practically the same, confirming Küster's views. *W. D. B.*

New Experiments on the Precipitation of Metals. *J. B. Senderens. Bull. soc. chim. Paris*, **17**, *271* (*1897*). Nickel does not act upon silver and copper sulfates or upon the acetates of silver, copper and lead whereas cobalt precipitates silver and copper. Antimony precipitates silver very slowly and copper even less rapidly. The author has studied the precipitation of metals by metals very thoroughly and his results deserve careful study. He finds that in almost no case does exactly one equivalent go into solution for one equivalent precipitated. It is to be noticed however that a couple is formed by the precipitation of one metal upon another and that the disturbing effects due to this should be taken into account.

W. D. B.

Alloys of Cadmium with Silver and Copper. *J. B. Senderens. Bull. soc. chim. Paris,* **15**, *1241* (*1896*). If a stick of cadmium be plunged into a solution of silver sulfate or acetate, silver is first precipitated and then takes up cadmium, apparently forming the compound $AgCd_2$. With copper sulfate there seems to be formed a solid solution of cadmium and copper. *W. D. B.*

On the Electrolytic Condition, *etc. G. Carrara. Gazz. chim. Ital.* **27**, *I, 89* (*1897*). Reviewed in this Journal **1**, 452; from Zeit. phys. Chem. **21**, 680 (1897).

A Method of Measuring Conductivity, *etc. W. Stroud and J. B. Henderson. Proc. Phys. Soc. Lond.* **15**, *13* (*1897*). Reviewed in this Journal **1**, 450; from Phil. Mag. [5] **43**, 19 (1897).

Structure Phenomena

Dimorphism of the Succinates of Camphol α; Isomorphism of the Succinates of Camphol α and of Isocamphol β. *J. Minguin. Comptes rendus,* **124**, *86* (*1897*). The optically active succinate of camphol α crystallizes from petroleum ether in hexagonal plates; from methyl alcohol in orthorhombic prisms. A mixture of optically active camphol α and isocamphol β crystallizes always in hexagonal plates and the specific rotation varies with the relative proportions of the components. *W. D. B.*

New Method of obtaining Transparent Crystals. *C. de Watteville. Comptes rendus,* **124**, *400* (*1897*). « If a crystal be rotated while growing it will assume a transparency and brilliancy similar to that of cut gems ». The method is a good one but not new. *W. D. B.*

Structure Isomerism and Rotary Power. *P. A. Guye and J. Guerchgorine. Comptes rendus,* **124**, *230* (*1897*). From a study of fourteen esters the authors conclude that the propyl group is heavier than the isopropyl, the isobutyl than the normal butyl and the latter than the secondary butyl. *W. D. B.*

Isomerism of Position and Rotatory Power. *P. A. Guye. Bull. soc. chim. Paris.* **15**, *1157* (*1896*). On reviewing various experimental researches, the author finds confirmation for the conclusion that para derivatives are usually more active than corresponding meta compounds, and these more active than the ortho compounds. The introduction of the methyl group into the benzene nucleus of an active body may either increase or diminish the rotatory power, according to the position of this methyl group with reference to the primary substituted chain and according to the groups of active bodies concerned. Theories regarding the center of gravity of asymmetric groups, see Franklin and Wharton, Jour. Chem. Soc. **69**, 1309, this Journal **1**, 196, are subjected to some reservation.

R. B. W.

Influence of Temperature on the Specific Rotation. *P. A. Guye and E. Aston. Comptes rendus,* **124**, *194* (*1897*). Eighteen optically active liquids were studied and with each a decrease in the specific rotation was noticed with rising temperature. This makes fifty substances in all for which this change has been shown.

W. D. B.

Dissociation Spectra of Melted Salts. *A. de Gramont. Ann. chim. phys.* (*7*) **10**, *214* (*1897*). The melted haloid salts all showed the lines of the halogen. *W. D. B.*

On the Fluorescence-Spectrum of Sodium. *E. Wiedemann and G. C. Schmidt. Verh. phys. Ges. Berlin,* **16**, *37* (*1897*). The fluorescence spectrum is very similar to the absorption spectrum, consisting of the D line, a band in the red and a series of bands in the green and blue. *W. D. B.*

Determination of Index of Refraction of Organic Liquids from the Molecular Formula and the Specific Gravity. *H. Staigmüller. Stuttgart, 1896.* Instead of the usual formula for the molecular refraction, the author proposes the following where $p =$ reacting weight and $S =$ molecular coefficient (Molekularpotenz):.

$$S = \left[\left(\frac{n-1}{d}+1\right)^{2} - 1\right] p$$

The author then shows that the index of refraction can be calculated from the knowledge of the values for the elements. *W. D. B.*

The Refraction Constants of Crystalline Salts. *W. J. Pope. Jour. Chem. Soc.* **69**, *1530* (*1896*). The author collates and discusses many experimental data. In order to apply Gladstone's formula (molecular refraction $= V(r - 1)$, where $V =$ molecular volume) to anisotropic media, $\sqrt[3]{\alpha\beta\gamma}$ or $\sqrt[3]{o^2e}$ may be substituted for r, where α, β, γ are the three principal refractive indices, or o is the ordinary and e the extraordinary refractive index. For convenience, the arithmetical means are substituted for geometric, making $r = \frac{1}{3}(\alpha + \beta + \gamma)$ or $\frac{1}{3}(2o + e)$.

Molecular refractions for bodies in the solid and liquid conditions are not directly comparable; for example, the values for ice at 0° are about one percent higher than for water at 20.2°.

A table of 115 salts, representing five crystalline systems, shows that the molecular refractions are practically additive quantities, which may be calculated with fair approximation from refraction constants which the author tabulates, and which are quite different from those previously deduced from observations made on solutions.

R. B. W.

The Refraction Constants of Crystalline Salts. *A. E. Tutton. Jour. Chem. Soc.* **71**, *235 (1897)*. A detailed statement to the effect that Pope's ideas and arithmetic are both inexcusably weak, Jour. Chem. Soc. **69**, 1530 (1896). See above review. *W. D. B.*

On the Changes of Color of Certain Salts under the Action of Cathode Rays. *E. Goldstein. Sitzungsber. Akad. Wiss. Berlin*, **1895**, *467; Wied. Ann.* **60**, *491 (1897)*. The salts were mainly haloids of Na and K. Exposure of the powdered salts to the cathode rays causes changes in color. The salts are shaken during exposure so as to make the change uniform throughout the mass. Exposure to the visible rays of the sun changes the colors back to their original values—sometimes through one or more intermediate stages. The changes take place more slowly in the dark, and more rapidly at higher temperatures whether in the light or not. The changes are irreversible as regards temperature except for one intermediate color of NaCl. In some other respects NaCl offers exceptions to the general statements above: its changes in the dark are, for instance, inappreciable at ordinary temperatures. *E. B.*

On Pleochroism in Vegetable and Animal Fibres which have been colored with Silver and Gold Salts. *H. Ambronn. Ber.*

sächs. Akad. Wiss. **48**, *613* (*1896*). If silver chlorid be precipitated in vegetable fibres and exposed to the light, no pleochroitic coloring occurs. If dry silver nitrate be dusted over the fibres and exposed to the light, the color spreads gradually in concentric circles from the crystal, showing marked pleochroism. The moisture of the air is essential since no effect is produced in a desiccator. The same effect is produced with many animal fibres and with gelatin in a state of tension, while gold chlorid may be substituted for silver nitrate. The author inclines to the idea that in some way the metals are precipitated in crystalline form with definite arrangement and cites, as analogous, Kundt's experiments on the precipitation of metals on a glass plate by electrical discharges. Kundt found that the film showed double refraction. The author calls attention to the fact that we know as yet no reason why silver from silver chlorid and silver nitrate should behave differently. A possible analogy is to be found in allotropic silver which has very different properties depending on the solutions from which it is precipitated. *W. D. B.*

The Present State of the Solarisation Problem. *J. Raphaels. Phot. Archiv*, **1897**, 4. The author points out that we do not know whether the appearance of a positive on over-exposed plates is due to the change in the silver salts or to an effect of the developer. He cites experiments in favor of both views. *W. D. B.*

The Grain of Dry Plates. *R. E. Liesegang. Phot. Archiv.* **1897**, 1. Schumann found that addition of potassium bromid to the developer increases the size of the metallic silver particles in the negative. It is an open question whether this is due to the potassium bromid dissolving the silver bromid, to the development being slower, or to some other cause. Ostwald ascribes the increase in sensibility of gelatin plates with time as due to gradual formation of a compound made up of silver bromid and gelatin. Whether this be true or not, it is certain that the gelatin is necessary to the formation of a picture. *W. D. B.*

On the Employment of Aldehydes and Acetones in Presence of Sodium Sulfite for the Development of the Latent Photographic Image. *Lumière Bros. and Seyewetz. Bull. soc. chim. Paris*, **15**, *1164* (*1896*). The authors attribute the action to the formation of the bisulfite compound and the sodium salt of the aromatic alcohol. In confirmation they show that when solutions containing pyrogallol or hydroquinone and acetone are shaken with ether less of the reducing agent passes into the ether phase if sodium sulfite be added to the solution. *W. D. B.*

Law of the Transparency of Gases for the X-rays. *L. Benoist. Comptes rendus*, **124**, *146* (*1897*). For sulfurous acid, methyl chlorid and air at the same pressure and temperature the specific absorption is a constant. *W. D. B.*

Electric Shadows and Luminescence. *S. P. Thompson. Chem. News.* **75**, *103, 111, 122, 134* (*1897*). A report of the progress which has been made in the study of the X-rays; delivered as a lecture before the Royal Institution. *J. E. T.*

On the Actual Existence of Hall's Phenomenon in Liquids. *H. Bagard. Nuovo Cimento* (*4*) **4**, *383* (*1896*). The author replies to the objections raised by Florio, Nuovo Cimento (4) **4**, 106 (1896), showing that Florio used small electrodes dipping directly into the liquid film, instead of large ones connected indirectly. *W. D. B.*

On the Measurement of the Dielectric Constant of Small Quantities of Substance by Means of Electric Waves in Wires. *P. Drude. Ber. sächs. Akad. Wiss.* **1896**, *583*. The end condenser of a Lecher system is made of two small platinum electrodes in a very small flask so that ¼ cc is enough to fill the condenser. The distance to the bridge (for maximum resonance) depends on the dielectric constant of the liquid. The bridge is kept fixed and the wires between it and the condenser are changed in length till there is a maximum of light in a vacuum tube placed across the parallel wires $\lambda/4$ from the bridge and between it and the condenser. The apparatus is calibrated by liquids of known dielectric constants, after which the constant for any new liquid may be read off from the curve of calibration. The accuracy is, in general, one to two percent. The greater part of the paper is devoted to a theoretical discussion of the method, for which we must refer to the original. *E. B.*

On the Capillarity Constants of Molten Metals. *H. Siedentopf. Inaugural Dissertation. Göttingen* **1896**. The method used was that of measuring the curvature of a drop, carbonic acid being substituted for air. Observations were made upon mercury, tin, lead, cadmium and bismuth. From the Eötvös equation one must conclude that all these metals are associated in the liquid state. The values of the capillarity constants for alloys of tin and bismuth are a linear function of the values for the two components. The capillarity constant for mercury at 16° is 45.4 mg/mm. *W. D. B.*

Empirical Formulae for Viscosity as a Function of Temperature. *A. W. Duff. Phys. Rev.* 4, *404* (*1897*). A discussion of seven empirical formulas and a comparison with experiment. The paper is of interest to those who are forced to deal with viscosity. *E. B.*

The Atomic Refraction of Carbon, Hydrogen, Oxygen and the Halogens. *J. Traube. Ber. chem. Ges. Berlin*, 30, *39*(*1897*). In Brühl's paper on the recalculation of atomic refractions, Zeit. phys. Chem. 7, 140 (1891), the value 4.570 for the refractive equivalent of the group CH_2 (hydrogen line *C*; n^2 formula) is obtained from observations on sixty-five saturated aliphatic substances. By excluding the earlier members of the homologous series (by reason of their tendency to «association») and by taking account of the benzene derivatives and of determinations published since the date of Brühl's paper, Traube reaches the conclusion that this number is too small, and should be at least 4.64. The following table shows the change necessitated by this alteration.

	CH_2	O′	O″	O_2	H	C	|=	|≡
Brühl	4.570	1.518	2.326	1.655	1.103	2.365	1.836	2.22
Traube	4.64	1.51	1.96	1.57	0.98	2.68	1.49	1.82

	Cl	Br	I
Brühl	6.014	8.863	13.808
Traube	6.00	8.79	13.74

The symbol |= indicates double bond between two Catoms.
W. L. M.

Spectrometric Determinations. *J. W. Brühl. Ber. chem. Ges. Berlin* 30, *158* (*1897*). Determinations of the refraction and dispersion of ethyl oxid, methylal, orthoformic ether, orthocarbonic ether, hydrazin *as*-dimethyl-hydrazin, *n*-butyl-methylamine, for the purposes of the paper following. *W. L. M.*

Hydrazine, Hydrogen Peroxide, and Water. *J. W. Brühl Ber. chem. Ges. Berlin*, **30**, *162* (*1897*). From the constitutional formulas usually assigned to the substances in question, it follows that the optical relations between the members of the series, nitrogen, ammonia, hydrazin should be paralleled by those between oxygen, water, hydrogen peroxid. This is not the case; the molecular refractions of ammonia, hydrazin and members of the hydrazin group are practically identical with values calculated from the (atomic refractions) of hydrogen and of the amino group (NH_2), *i. e.*, the atomic refraction of nitrogen is the same in all. That of oxygen on the other hand is least in water, intermediate in value in hydrogen peroxid and greatest in the case of gaseous and of liquid oxygen.

As the formula of hydrazin usually adopted, $H_2N \cdot NH_2$, is in agreement with its chemical and spectroscopic behavior, an alteration must be made in the formula of hydrogen peroxid—the author suggests HO ⋮ OH. The molecular constitution of oxygen gas also must be essentially different from that of nitrogen: the author however considers it premature to offer a suggestion as to the probable nature of this difference. *W. L. M.*

Artificial Coloration of Crystals of the Haloid Salts of the Alkalies. *F. Giesel. Ber. chem. Ges. Berlin*, **30**, *156* (*1897*). Goldstein has observed that the salts in question are superficially colored by exposure to the cathode rays, Wied. Ann. **54**, 371 (1895); the author finds that crystals of one centimetre in diameter may be colored throughout their mass by heating to a dull red heat in the vapor of sodium or potassium.

The colored crystals are clear and transparent, the color is permanent in the air but on exposure to high temperatures is changed and finally destroyed. With water colorless solutions are formed, which on evaporation deposit colorless crystals. The author points out the analogy between the behavior of his artificially colored crystals, and that of naturally occurring rock salt. *W. L. M.*

Circular Polarization and Symmetry of Structure. *W. Barlow. Phil. Mag.* [*5*] **43**, *110* (*1897*.) The author compares "the various distinct classes of cases in which circular polarization occurs, with the geometrical possibilities for homogeneous structure unbroken and broken, *i. e.* for substances both in the crystalline and fluid conditions.» Taking as a starting point «the very obvious conclusion that since circular polarization is essentially an enantiomorphous property, if it is traceable to an arrangement of the parts the structure in which it occurs must be enantiomorphous» he finds that «exactly corresponding to the five classes into which substances that possess the power of converting plane polarized light into circularly polarized light can be divided, there are five classes of structure distinguishable by characteristic geometrical features»; and concludes that «it can hardly be doubted that circular polarization is a mechanical effect depending on the relative situation of the ultimate particles of bodies, and that the disappearance of the property, and the change in it observed when the state of a body displaying it alters, are also mechanical effects entirely due to changes in geometrical configuration.» *W. L. M.*

Water of Crystallization. *Th. Salzer. Pharm. Ztg.* **41**, *846* (*1896*). Salts of acids whose stereochemical formulas represent the carboxyl groups as close together, crystallize with little or no water. The author illustrates his theory by comparing the salts of malonic and succinic acids with those of their substitution products, and by reference to the regularities in the water of crystallization of salts belonging to the glycollic and acrylic series, *etc.* *W. L. M.*

Optical Rotation in the Crystalline and Amorphous States. *H. Traube. Jahrb. für. Min.* **10**, *Beilageband 788* (*1896*). Measurements on (*a*) patchouli-camphor, (*b*) laurineen-camphor, (*c*) matico-camphor, (*d*) rubidium tartrates, (*e*) calcium tartrates. In some cases (*a*, *b*) the molecular rotation in the amorphous state is the same as that of the crystals; in others (*c*, *d*) less. The direction of the rotation may be different for crystal and aqueous solutions (*d*, *e*). *W. L. M.*

THE VARIANCE OF OSMOTIC SYSTEMS

BY J. E. TREVOR

Let us imagine a solution and a mass of the corresponding pure solvent contained in two vertical cylinders which have in common a semipermeable wall, impermeable for the solute, and each of which carries a movable piston. The mutual attraction of the two substances, whereby a homogeneous solution is formed when they are brought together, tends to draw solvent through the separating wall into the solution, a tendency which may be counterbalanced by an increased pressure upon the solution—the osmotic pressure of the system. By regarding the osmotic pressure in this simple and direct manner, instead of conceiving it to be an expansive force of one component alone, of the solute, we are freed from the necessity of thinking that this supposed inner pressure will push up the free upper surface of the solution in an osmotic tube, and we come to the rational conclusion that the osmostic pressure only exists when there is an actual separation of mutually attracting components. The osmotic pressure, namely, is best conceived as the equilibrium pressure upon the solution side of such a system.

I have shown in an earlier paper[1] that in osmotic systems of the type described the appearance of two different equilibrium pressures, one upon each side, gives an increase, by one, in the number of the thermodynamic variables which appear in the ‹fundamental equations›[2] of the phases of the system, and that accordingly the variance of these systems is greater by unity than if the separating osmotic wall were absent. The variance v, therefore, when n independently variable components are present in r phases is

$$v = n + 3 - r$$

instead of $n + 2 - r$, as in the more usual case. Thus $(n + 1)$-phase

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[1] This Journal **1**, 349 (1897).

[2] In Gibbs's sense.

systems become divariants, ($n + 2$)-phase systems are monovariants and the nonvariants contain $n + 3$ phases. In the simple two-component systems we must find sets of five phases coexisting in nonvariant equilibria at the multiple points—five-fold points,— and we are thus led to anticipate the possibly of representing, for any such system, at least one set of five monovariant curves of osmotic equilibrium pressures, running into a corresponding five-fold point. To indicate the manner in which this anticipation may be realized is the object of the present note.

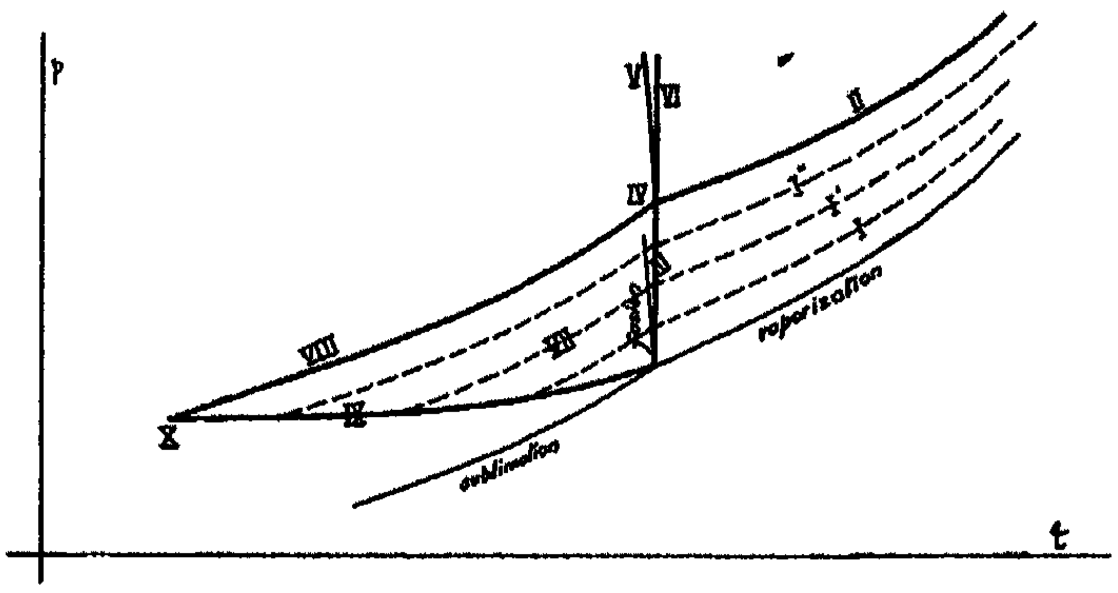
In order to simplify the discussion let us suppose the two components to be water and a salt. We may then suitably start from water alone, whose vaporization, sublimation and fusion curves in the temperature-pressure plane are represented by the three fine lines of the subjoined diagram. The figure is not drawn to scale.

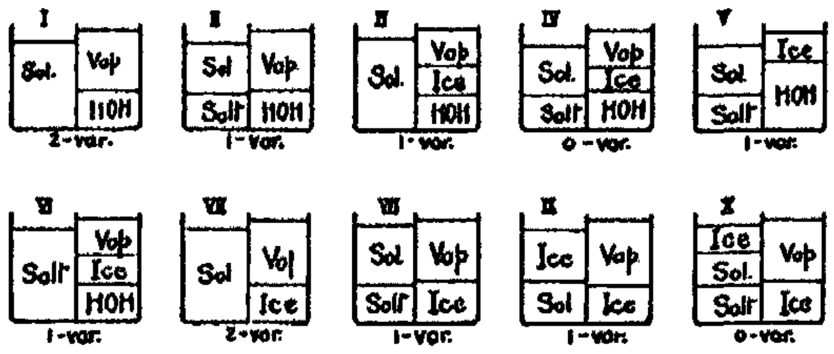
I. Setting out with pure water in both cylinders the first result of adding salt to one, say to the left one, will be to increase the pressure necessary there to hold the system of phases in equilibrium. At any given concentration of the solution we shall thus have an osmotic pressure which will vary with the temperature as represented, for example, by some one of the dotted curves marked I in the diagram. The concentration, and consequently the pressure, being variable at constant temperature, and the temperature being independently variable also, the system is seen to be divariant,—as indeed it should be since it has $n + 1$, or 3, phases.

II. When enough salt is added to form a saturated solution, with the excess precipitated, it becomes no longer possible to vary the concentration and the equilibrium osmotic pressure of the system of phases at constant temperature; the pair of equilibrium pressures will vary however with varying temperature, the osmotic pressure curve becoming that numbered II in the diagram. The system is monovariant,—it has actually four, or $n + 2$, phases.

III. Had we started from pure water at zero centigrade with ice present, the addition of salt would have melted the ice upon the solution side at this temperature, so that with increasing concentration of salt we should have a rising osmotic equilibrium pressure with unchanging temperature, until the point of saturation with respect to the salt is reached. This equilibrium is the four-phase monovariant, III.

IV. The precipitation of salt adds a fifth phase to the system and decreases the variance to zero, for the concentration of the saturated solution is invariable and the temperature can not be changed without melting the phase of ice. We here find our expected $(n+3)$-phase nonvariant system. This state of affairs might also be reached by cooling the monovariant system II until ice appears in the right hand compartment,—so both curves run into the multiple point IV.





V. An increase of pressure upon both sides of the system as it now stands will condense the phase of saturated vapor and drive the fusion equilibrium along the fusion curve of the solvent, thereby lowering the temperature and requiring the osmotic equilibrium pressure to increase at the exact rate necessary to keep the solution in osmotic equilibrium with the water phase. The osmotic pressures follow the curve V, corresponding to this four-phase monovariance.

VI. If, on the other hand, we increase the pressure upon the solution side only, we shall drive the water from the solution through the wall and have remaining there the salt alone. The pressure can then be varied at will upon the salt, but the temperature can not be changed because of the mass of ice present upon the other side, so the system is again monovariant; this four-phase system corresponds to the equilibrium curve VI.

VII. Returning to the curve III it is clear that if from the state represented by any point upon it the temperature be lowered without varying the concentration of the solution the phase of water will become ice, and the osmotic pressure, to maintain the solution in equilibrium with this ice, must follow one of the dotted pressure curves VII which sweep out the corresponding divariant field. The concentration is of course also independently variable, as well as the temperature. Another series of $(n+1)$-phase divariant systems thus appears.

VIII. With the appearance of saturated solution and the consequent precipitation of an excess of salt we arrive at another equilibrium, variant only with the temperature; the monovariant VIII, which affords the expected fifth monovariant curve running into the five-fold multiple point IV. The same curve would be traversed through a simple cooling of the nonvariant system, whose phase of liquid water would thus be made to disappear.

IX. Continued cooling of any of the divariants VII will in each case eventually give rise to the appearance of ice in the unsaturated solution at the freezing temperature of the latter; the equilibrium will then remain monovariant because of the change of concentration with the varying temperature, and we thus get the $(n+2)$-phase equilibrium which is represented by the curve IX.

X. A continued increase of salt-concentration, up to saturation, will reduce the variance to zero again, giving the $(n+3)$-phase (five-phase) system of the multiple point X. This occurs at the freezing temperature of the saturated solution on the osmotic side, and can accordingly be reached by a cooling of the monovariant system VIII. Curves IX and VIII are therefore two of the set of five running into this second five-fold point. A further discussion of the equilibria here would be relatively uninteresting, because of the frequent absence of the phase of solution with its varying concentration.

Thus, for two-component monovariant systems may be realized the anticipated set of five curves of osmotic pressures, and their intersection at a five-fold multiple point.

Cornell University

MASS LAW STUDIES, III

BY S. F. TAYLOR

In a previous paper[1] I have communicated some measurements on the coexisting liquid phases for benzene, water and alcohol at 25° and have discussed the quantitative relations which hold along the isotherm. The study of such systems is made much easier if one makes use of a triangular diagram in representing the results. The advantages of this have already been pointed out clearly by Stokes[2] but his note seems to have received little or no attention and for this reason it seems worth while to bring the matter to the front again.

My results are therefore reproduced graphically in the cut, the concentrations being given as synthetic volume concentrations. The field for unsaturated solutions lies outside of the curve while the field inside or below the curve represents supersaturated solutions. Any mixture having a composition represented by any point in this field will separate into two solutions represented by two points on the curve. Stokes has proposed calling the two coexisting liquid phases «conjugate» solutions and I shall use the word in this sense. In the diagram straight lines are drawn connecting the conjugate solutions so far as I have determined them.[3] These connecting lines were called «tie-lines» by Stokes. If we take varying quantities of two conjugate solutions the compositions of the resulting mixtures will lie on the tie-line for that pair of conjugate solutions. Reversing this we may say that any mixture represented by a point on a tie-line will separate into the two conjugate solutions at the

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[1] Jour. Phys. Chem. **1**, 461 (1897).

[2] Proc. Roy. Soc. **49**, 174 (1891).

[3] The tie-line for solution I is omitted because it can not well be shown in a diagram of this size.

ends of that line and that the relative amounts of the two liquid phases will be given by the ratio of the distances from the point to the ends of the line. One can also use this as a check on the results.

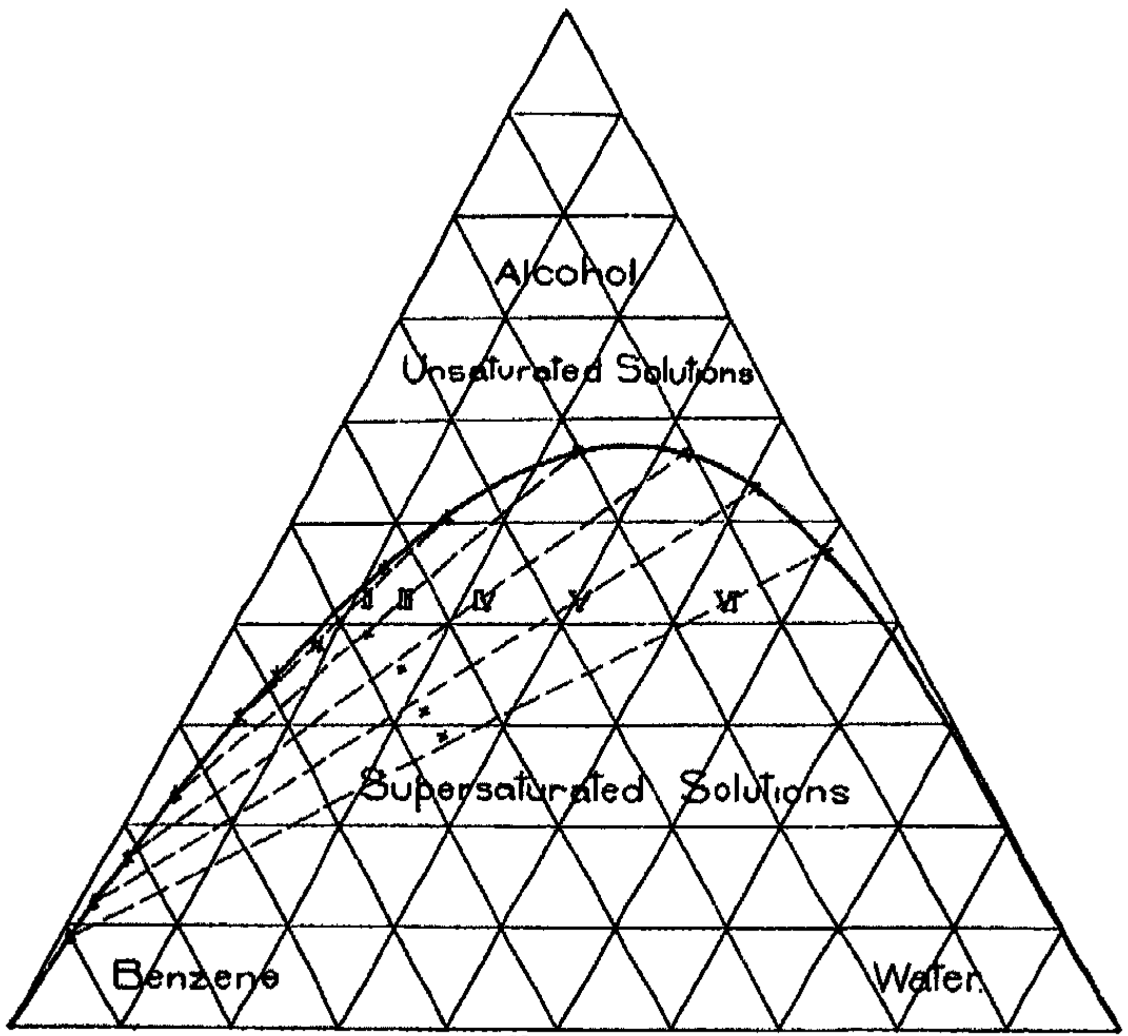

FIG. 1.

In the preceding paper on this subject there is an analytical comparison of the actual compositions of the mixture taken and the values calculated from the conjugate solutions.[1] At the time it was remarked that the method was unsatisfactory because one had the choice of concentrating the error in one component or of distributing it over the three, neither of which is really satisfactory. By representing the results graphically it can be seen at once whether the

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[1] An error has crept into Table VIII, page 436, for which I am personally responsible. The calculated value for water in series I should be *1.52* instead of *1.63*. By an oversight some of the "found" solutions in this table were given as they were made up and not reduced to twenty cubic centimeters. If this were done it would involve slight changes in Table VII but would not affect the relations perceptibly in either table. W. D. B.

value for the original mixture falls upon the tie-line or not. In the diagram I have marked the compositions of the original mixtures. It will be noticed that the result is unsatisfactory in the case of solution I where the point lies on the tie-line for solution II instead of on the proper one and that in all the cases the experimental error is large. The fact that a straight line through the point for one conjugate solution and the point for the system as a whole cuts the curve at the composition for the other conjugate solution makes it unnecessary to analyze both liquid phases when the data for the curve are already known and the results thus obtained can be checked by taking any other mixture represented by a point on the tie-line and showing that it gives the same upper or the same lower phase whichever is the more convenient.

Stokes calls attention to a property of conjugate solutions which seems to have been considered very surprising at the time. He points out that the final equilibrium depends only on the compositions of the upper and lower mixtures and not on their quantities. This point was taken up by Wright, Leon and Thompson[1] who came to the conclusion after many experiments that this proposition was a correct one. It is interesting to notice that in 1891 it was not recognized that this proposition was merely a special case of the more general one that the absolute mass of the phase has no effect upon the equilibrium when all disturbing influences are removed.

In the course of the experiments referred to, Wright, Thompson and Leon determined the compositions of certain pairs of conjugate solutions for the system, chloroform, water and acetic acid. Their data are given in Table I.

A single glance at this table is enough to show that the results are not absolutely accurate. Pure chloroform will not take up one percent of water. Addition of acetic acid can not cause the amount of water in the chloroform to fluctuate in the remarkable manner indicated in the table. For this reason it was not worth while even to attempt to apply the mass law to the single phases. On the other hand it seemed probable that the amount of acetic acid in the two phases might have been measured with a fair amount of accuracy,

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[1] Proc. Roy. Soc. 49, 178 (1891).

TABLE I

Lower layer			Upper layer		
$CHCl_3$	H_2O	CH_3CO_2H	$CHCl_3$	H_2O	CH_3CO_2H
99.01	0.99	0.00	0.84	99.16	0.00
98.24	0.72	1.04	0.92	92.62	6.46
94.98	1.19	3.83	0.79	81.52	17.69
91.85	1.38	6.77	1.21	73.69	25.10
91.23	0.82	7.95	1.85	70.42	27.73
87.82	1.13	11.05	2.97	63.32	33.71
80.00	2.28	17.72	7.30	48.58	44.12
72.86	3.62	23.52	12.82	37.82	49.36
70.13	4.12	25.75	15.11	34.71	50.18

since it was determined by titration. In that case it should be possible to describe the distribution of acetic acid between the two phases with a fair degree of accuracy for all except the more dilute solutions. If we express the concentration of the acetic acid in the lower phases in terms of a constant quantity of chloroform and in the upper phase in terms of a constant quantity of water, the equilibrium should be described by an equation of the form :

$$m \log z_2 - \log z_1 = \log C$$

where z_2 and z_1 are the mass concentrations of acetic acid in the lower and upper phases respectively while m is a constant but not necessarily an integer. This proves to be the case and the results are given in Table II. In the first two columns are the values for acetic acid in the lower and upper layers, referred in the one case to one hundred grams of water. In the third column are the values for acetic acid in the upper layer referred to one hundred grams of water. In the third column are the values for acetic acid in the upper layer referred to one hundred grams of water and calculated by means of the equation :

$$0.88 \log z_2 - \log z_1 = 0.225 - 1$$

In the fourth column are the grams of acetic acid in one hundred grams of the aqueous solution, while the fifth column gives the product of the third column into the fourth column of Table I,—to all intents and purposes the calculated amounts of acetic acid in one hundred grams of solution.

TABLE II

z_2	z_1	$z_1$calc.	found	calc.
1.1	7.0	6.3	6.5	5.8
4.0	21.7	20.3	17.7	16.6
7.4	34.1	34.6	25.1	25.5
8.7	39.4	40.0	27.7	28.2
12.6	53.2	55.2	33.7	35.0
22.1	91.0	91.0	44.1	44.2
32.3	130.3	127.1	49.4	48.1
36.7	144.5	144.2	50.2	50.0

It is of course fairer to compare the fourth and fifth columns rather than the second and third because the experimental error is magnified unduly in the latter case. The agreement is excellent with all save the two most dilute solutions and there the discrepancy is unquestionably due to experimental error.

Cornell University

SOLUBILITY OF SOLIDS IN VAPORS

BY J. M. TALMADGE

The solubility of solids in vapors has been a subject of some little comment in the last few years, many chemists holding that such a phenomenon is impossible and that any apparent increase in the amount of the solid component in the vapor phase is due to particles of the solid being carried up mechanically by the vapor or to drops of solution being held in suspension in the same way. Since most of the experiments, that have been made heretofore, have been qualitative in nature, the object of this paper is to give the results of a series of quantitative determinations of the concentrations of the distillates obtained when saturated solutions of camphor or naphthalene in methyl alcohol, ethyl alcohol, acetone or ether are distilled under different pressures. From these data it will be possible to determine whether the nature of the solvent has an appreciable effect upon the amount of the solute carried over.

The method adopted was practically that used by Ramsay and Young in their determinations of vapor pressures by sublimation and distillation.[1] A 250 cc distilling flask was used, on the arm of which was placed a small condenser. This was connected with a second distilling flask which acted as a receiver and which was placed in ice or cold water. The receiver was connected with a mercury manometer and the suction pump. In all cases an excess of the solid was present in order to avoid supersaturation. The solution was heated slowly upon a water bath until the desired temperature was reached ; the pump was then started and shut off when the solution began to distil. The pressure under which the liquid boiled was read off from the manometer, while the temperature was

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[1] Phil. Trans. **175**, 37 (1884).

given by a thermometer, the bulb of which was immersed in the distilling liquid. The temperature of the distillate was not noted since that has no direct bearing upon the results. In order to prevent superheating, the temperature of the water bath was kept only a few degrees above that of the boiling solution. With a little practice it was found easy to carry on the distillation at constant temperature.

The acetone used was purified by treating with calcium chlorid and subjecting to fractional distillation; the ethyl alcohol by treating with anhydrous copper sulfate and quicklime. The ether was dried over sodium and distilled, while the methyl alcohol was purified by fractional distillation. The naphthalene was crystallized from ninety percent alcohol and the camphor from fifty percent alcohol.

The distillates were analyzed with the refractometer, the relation between concentration and index of refraction having been determined from measurements made from known solutions, the results being represented graphically. The readings with the refractometer were all made at 21°.

In Table I are the measurements with naphthalene in the four solvents. The first column gives the boiling-point; the second, the pressure in millimeters of mercury; the third, the grams of naphthalene in ten grams of the solvent as determined by analysis; while in the fourth column are the vapor pressures of the naphthalene, calculated on the assumption that the vapors of the two components follow the gas laws. This, of course, is an assumption which is probably not accurate in any one case; but, on the other hand, it is the only one that can be made and the variations undoubtedly lie within the probable error of the measurements which is about five percent. In any case this would not have any appreciable effect upon the relative amounts of napthalene which pass over with different solvents. The formula used in calculating the results is

$$\frac{g/M_1}{g/M_1 + 10/M_2} P = p$$

where g is the number of grams of naphthalene in ten grams of the solvent, M_1 the reacting weight of naphthalene, M_2 the reacting weight of the solvent, P the pressure as given by the manometer and p the partial pressure of the naphthalene vapor.

TABLE I

Naphthalene and Ether

Temp.	Press.	Conc.	V. P.
25°	448	0.076	2.0
35	471	0.083	2.3
37	509	0.089	2.6
51	731	0.101	4.2
56	745	0.109	4.7
Napthalene and acetone			
43	468	0.090	1.9
45	508	0.097	2.2
Naphthalene and methyl alcohol			
57	497	0.447	5.5
60	522	0.474	6.1
66	538	0.521	6.9
Naphthalene and ethyl alcohol			
51	220	0.085	0.7
59	300	0.145	1.6
67	430	0.18	2.8

It will be noticed that the highest vapor pressure which I have found is just under seven millimeters. I have been unable to verify Benedict's measurement with naphthalene and ether[1] and it seems certain that there must be a very serious error in that determination. The discrepancy between the two sets of results is so large as to lead one to suspect a misplaced decimal point in the calculation of the results.

Since there are no direct determinations of the vapor pressures of solid naphthalene, it is impossble to say whether or not the partial pressures recorded in Table I are abnormally high. We can, however, compare these results among themselves in order to see whether the nature of the solvent has an effect upon the apparent partial pressure of the naphthalene. In Table II are tabulated the results for the different solvents at the same temperature as far as this is possible, the data being obtained by graphical interpolation.

[1] Jour. Phys. Chem. 1, 397 (1897).

The solvents to which the figures refer are given at the heads of the columns.

TABLE II

Temp.	Ether	Acetone	M. Alcohol	E. Alcohol
43°	3.2	1.9		
45	3.5	2.2		
51	4.2			0.7
56	4.7			1.2
57			5.5	1.3
59			6.0	1.6
60			6.1	1.7
66			6.9	2.6

It will be seen at once that the nature of the solvent is of great importance, the values with ether being much higher than those with acetone, while methyl alcohol raises the apparent partial pressure of naphthalene much more than ethyl alcohol does. Since the values vary with the solvent, they can not all be equal to the vapor pressure of naphthalene when no solvent is present. While these experiments show that the concentration of naphthalene vapor in equilibrium with solid naphthalene is not independent of the other components in the system, they do not show whether the vapor pressure is increased or decreased by the presence of a solvent.

This question can best be answered by a study of the behavior of camphor with the same four solvents. The results of the experiments with camphor are given in Table III, the data being tabulated in the same form as in Table I.

The most casual inspection of these figures shows that here, as with naphthalene, the vapor pressure of the solute varies with the solvent. The relation of these vapor pressures to those obtained by direct measurement is shown in Table IV. In the second column, under the heading of R. and Y. are the values obtained by interpolation from the data of Ramsay and Young.[1] In the acetone column the values for 58° and 71° are obtained by interpolation.

There can be no question as to the results. The values with ether and acetone are more than double the real vapor pressures. With

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[1] Phil. Trans. 175, 45 (1884).

TABLE III

Camphor and Ether

Temp.	Press.	Conc.	V. P.
50°	488	0.38	8.9
Camphor and acetone			
52	371	0.604	8.4
61	511	0.644	12.2
74	651	0.684	16.5
Camphor and methyl alcohol			
36	168	0.507	1.8
58	308	1.187	7.5
Camphor and ethyl alcohol			
71	345	0.308	3.4
86	510	0.418	6.7

methyl alcohol the values are a little above the normal, while with ethyl alcohol the calculated vapor pressures are only about one-half of those obtained directly. This last phenomenon was entirely unexpected but there seems to be no reason to question the accuracy of the figures. For the present there seems to be no satisfactory way of accounting for this result on theoretical grounds and it will be necessary to study the matter more thoroughly than has yet been done before offering any explanation.

TABLE IV

Temp.	R & Y	Ether	Acetone	M. Alcohol	E. Alcohol
36°	1.7			1.8	
50	3.6	8.9			
52	4.0		8.4		
58	5.0		11.1	7.5	
61	5.6		12.2		
71	7.7		15.3		3.4
74	8.5		16.5		
86	13.0				6.7

It is to be noticed that the order of the solvents is not the same with naphthalene and camphor. With the former the order was methyl alcohol, ether, acetone and ethyl alcohol; with the latter it is ether, acetone, methyl alcohol and ethyl alcohol; the difference between the two series being in the relative position of the methyl alcohol. With both solutes ethyl alcohol gives very much lower values than with any of the other solvents. Since there are as yet no solubility determinations for naphthalene and camphor in the different solvents, it is impossible to decide whether there is a relation between the solubility in the vapor and in the liquid.

There remains only the point in regard to the mechanical suspension of the solid or solution in the vapor. That is always a possibility and the present experiments throw no light upon the existence or amount of any error due to this cause. It seems, however, very improbable that this should be an important item. The regularity of the results with each solvent and the striking differences when one changes from one solvent to another are hardly to be reconciled with the conception of a more or less haphazard mechanical suspension. Such an explanation is negatived very effectively by the recent experiments of Villard[1] which have shown that the vapor pressures, both of solids and of liquids at ordinary temperatures, can be raised by presence at ordinary temperatures of a gas in which the substances are soluble. Villard found that if oxygen under two hundred atmospheres pressure was passed into a tube containing liquid bromin, the latter volatilized until the color in the vapor phase was much deeper than when the oxygen was not present. On decreasing the pressure, the color became paler and drops of liquid were formed on the walls of the tube. These drops redissolved when the pressure was increased. Under three hundred atmospheres pressure the color in the vapor phase was more intense than that of a solution of bromin in water and the author estimates that the concentration of bromin was at least six times that of the ordinary, saturated vapor. The increased volatility of bromin in an atmosphere of oxygen becomes noticeable to the eye when the pressure reaches four atmospheres. Iodin dissolves readily in oxygen though the phenomenon is not very striking at pressures less than a hundred atmospheres. Ethyl chlorid, carbon bisulfid and alcohol dissolve to any extent in methane, while iodin, camphor and paraffin

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[1] Jour. de Phys. (3) **5**, 453 (1896).

volatilize readily in it. On decreasing the pressure these solids crystallize upon the walls of the tube. At one hundred and fifty atmospheres, camphor and methane behave like two gases and seem to be miscible in all proportions.

These experiments of Villard are very striking in that they prove the increased volatility both of solids and of liquids. The first was to have been expected ; the second necessitates a change in our usual way of looking at things. Everyone has accepted heretofore the statement that dissolving one component in another lowered the vapor pressure of the latter. Apparently this will have to be modified so as to apply only to the cases in which the solute is practically non-volatile. When this is no longer true we shall have two effects working in opposite directions. We shall have the volatile solute dissolving in the solvent and lowering the partial pressure of the latter. On the other hand, the vapor of the solute will volatilize the solvent to a certain extent, thereby increasing the vapor pressure of the liquid. In open vessels only the first of these two influences is important, and it alone has been recognized. Under pressures of one or two hundred atmospheres, it becomes a minor matter and the increased volatility is the important item. The binary system, liquid and vapor, is more closely allied at high pressures to the binary system, two liquid phases, than to the binary system, liquid and vapor at low pressures. The analogy is with the solution of liquid phenol in water and not with the dissolving of phenol in water vapor. This brings up the point that since the critical pressure of oxygen is about fifty atmospheres at — 118°, oxygen under one hundred atmospheres at + 17° may be called liquid or gas as one pleases, in which case the analogy with the two liquid phases of phenol and water would be complete and there would be nothing remarkable in Villard's experiments and no reason to change any views that we now hold about the change of vapor pressure with the concentration. While this criticism may be a just one when applied to the experiments under one hundred atmospheres pressure, it does not apply to the observations made with oxygen under a pressure of four atmospheres and the conclusions will therefore have to stand.

As a further instance of the solvent action of vapors and gases, I may cite the experiments of R. W. Wood[1] on the solution of bromin and iodin in carbon bisulfid gas at 300°. It was found that when sufficient carbon bisulfid was present, the absorption spectra for the vapors of iodin and bromin disappeared and were replaced by the absorption spectra for the solutions of these substances. Wood has shown that, with increasing amounts of iodin or bromin, increasing density of carbon bisulfid gas is necessary in order to make the spectra of the vapors vanish and also that the ratio of the amounts of iodin and bromin for the same densities of carbon bisulfid are practically constant. It seems, therefore, impossible to avoid the conclusion that we are dealing with a solution of iodin or bromin in carbon bisulfid and not with a mixture of two gases.

Cornell University.

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[1] Zeit. phys. Chem. 19, 689 (1896).

COMMENT ON THE NOTE OF R. FRANCHOT ENTITLED «NASCENT HYDROGEN»

BY D. TOMMASI

I have just read a note by Mr. R. Franchot[1] entitled «Nascent Hydrogen». The author of this note seems to be entirely unaware of the fact that before him—in 1877[2]—I studied the question whether the reducing action of hydrogen when set free from a chemical compound is due to an allotropic form of hydrogen, such as the nascent state, or whether it is due to ordinary hydrogen evolved under new thermal conditions. To determine this point I examined the majority of the reductions caused by hydrogen and usually attributed to nascent action, such as: the reduction of the chlorid, bromid and iodid of silver; of the chlorates and perchlorates; of ferric chlorid; of the nitrates; of chloral, etc., etc. From these experiments I drew the conclusion that if hydrogen in the nascent state possesses a greater affinity than under the usual conditions, this is due simply to the fact that the gas, in separating from a compound, is accompanied by the quantity of heat which is produced while the hydrogen is being set free. Consequently, nascent hydrogen is nothing else than $H + x$ calories.

In an analogous way one can explain the greater activity of substances at the moment of liberation from their compounds, or in other words, when they are in the nascent state. My chief papers on nascent hydrogen have been published in the following Journals:

Rendiconti dell' Instituto Lombardo di Milano, (1877) and (1878); Chemical News, 1879; Cosmos-les-Mondes, Paris (1879): Bull. Soc. Chim. Paris **I**, 148 (1882). See also D. Tommasi: Traité des piles électriques.

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[1] Jour. Phys. Chem. **1**, 75 (1896).

[2] D. Tommasi. Traité théorique et pratique de l'électrochimie, 105.

NOTE

BY WILDER D. BANCROFT

Mr Tommasi's complaint that his work on nascent hydrogen had been overlooked by Mr Franchot is based on a misapprehension of the facts. It was in consequence of the very interesting results obtained by Tommasi that Franchot started on his work. It happened that so much time was wasted in discovering and eliminating the errors introduced by the direct action of the metal that the point was not reached at which one would naturally make a reference to Tommasi. The unfinished part of the paper included a study of Tommasi's hypothesis that nascent hydrogen is $H + x$ calories. If this represents the facts, there must be different amounts of reduction when zinc or copper is attacked by acids. This has not been shown conclusively to be the case nor has there been any careful study of the subject from the point of view of modern electrochemistry. There is therefore much interesting work to be done, starting from Tommasi's results. The papers of Tommasi, published in Italian, were known to me by title only since I have not yet been able to obtain copies of the originals.

NEW BOOKS

Vorlesungen über Theoretische Physik. *H. von Helmholtz; Band V, Vorlesungen über die Elektromagnetische Theorie des Lichts, herausgegeben von Arthur König und Carl Runge. Large octavo, 370 pages. L. Voss; Hamburg und Leipzig, 1897. Price 14 marks.* This is the first of the projected six volumes of Helmhotz's lectures to make its appearance. Helmholtz, as the editors tell us, was in the habit of improvising his lectures from a few introductory notes, a process which sometimes led to brilliant novelties, at other times however to insoluble results. Stimulating as this method was for mature students, it left with the younger men the almost insuperable burden of separating discarded premises from the continuity of the discussions. Helmholtz's papers and arguments even in complete form are usually tough reading, as the demonstrations are apt to advance, kangaroo-like, by leaps. It is well to bear these facts in mind in order to do justice to the book which the editors have issued,—a book which is thoroughly readable to a student moderately well acquainted with the electromagnetic theory of light. One might wish perhaps for a greater number of diagrams and a more frequent definition of variables, for instance when the investigation pauses temporarily at some definite result. One experiences some difficulty with novelties of notation, though these vanish naturally in the light of novelties of method. There is in particular a dearth of italicized or otherwise accentuated statements, so that the reader must accustom himself to follow a continuous argument and to do his own prodding. As to treatment, however, it seems to the writer that neither Lorenz nor Boltzmann nor Poincaré in dealing with this abstruse subject have been in like degree comprehensive and tangible.

Following a terse historical summary the book begins with a brief consideration of the differential equations for longitudinal and for transverse elastic plane waves, after which Maxwell's equations are deduced and eventually expressed in terms of the Laplacian operator. The short treatment of the potential function which follows is particularly marked in its discussion of Green's theorem, the importance of which Helmholtz further develops in other parts of the book. The first two sections conclude with a very full investigation of plane electric waves.

The less specialized case of spherical waves is next taken up with particular reference to Huyghens's principle, which is then exhaustively discussed Diffraction and geometric optics (the latter largely on Gaussian lines) follow naturally. Though less closely allied with the main subject, they are each treated with considerable detail.

In the closing chapters of the book, on polarization and dispersion, electromagnetics again come prominently to the front and in the latter instance we meet with regret the most recent of Helmholtz's great investigations. This section moreover is the only one which is in touch with physical chemistry, inasmuch as the propagation of an electromagnetic wave is dependent for its rate more particularly on the dielectric, to a smaller extent on the magnetic properties of the medium. In Maxwell's hands the electromagnetic theory had not yet suggested an explanation of dispersion, although the equations for the normal and tangential ether stresses were worked out. Helmholtz develops it in relation to the valency charges of the atoms. As it follows from Helmholtz's interpretations of Faraday's law, that the atoms of a molecule contain an equal number of contrary electrons, molecules so charged must be acted on by an alternating field after the manner of face couples. Without changing their mean positions, paired atoms move synchronously with the electric oscillations, either by vibrating around their centers of mass, or by changing their atomic distances in the molecule. Hence in transparent bodies there are added to the electric and magnetic moments due to the structure of the ether itself, the new electric moments of the paired (usually non-magnetic) ions. The accessory motions withdraw a part of the energy of the ether, change its oscillations and give rise to dispersion. The differential equations for this complex case are obtained somewhat abstrusely from Hamilton's principle. They are applied in deducing a law of dispersion[1] of remarkable generality, which explains anomalous refraction and predicts (as has since been pointed out) the absence of refraction and therefore also of reflection for rays of extremely small wave length, such as X-light is now usually believed to be. Kindred investigations of reflection and refraction, elliptic polarization, the motion of light in crystalline media including rotary polarization conclude the work. This last section requiring as it does thoroughgoing knowledge of dynamics and elastics is perhaps the most difficult, but in its novelty the most profoundly interesting part of a notable book.

Carl Barus

The Phase Rule. *W. D. Bancroft. Large octavo, viii and 255 pages. Published by the Journal of Physical Chemistry; Ithaca, N. Y. 1897. Price $3.00.* We have here a book which really fills a gap, in supplying from a single point of view a presentation of the wide field of the equilibria in heterogeneous systems.

This point of view is the phase rule of Gibbs. A better one, indeed any other—if it is to be applicable at all—does not exist. In the ten years which have elapsed since I myself drew up the first brief sketch of a classification according to this principle there has been raised upon it as a secure foundation an extensive structure wherein all conceivable equilibria have found place. After the recent conclusion of the extended labor which was necessary to fix the more prominent features of this work, the time became ripe for a new comprehensive exposition. I myself had planned to supply it, but was delayed in the execution; the work, however, has been undertaken by Bancroft and has been well carried through. He has been exceedingly successful in arranging the wealth of material according to the principle in question, in making clear the coherence of the phenomena and in presenting an inspiring picture of the imposing science of heterogeneous equilibria. Chemists, the majority of whom have as yet little acquaintance with this field, can now see with surprise to what remarkable development this new branch of our science has attained and what an excellent guide is the phase rule,

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[1] Ketteler, it will be remembered, has deduced the same law from the equations of the old elastic theory of light.

not only in supplying a general view of the whole but also in penetrating to the smallest details.

The chief difficulties lie in these details. It is especially through the manner in which the author has worked out many of them that I have learned how far he has gone in the comprehension of the principle and of its application. Nevertheless for most students it would have been better to have treated many of the details in footnotes.

The author has intentionally omitted all treatment of the quantitative side of the equilibria. Even without this the size of the book (255 pages) is great enough, and yet he has only discussed the three categories concerning which our knowledge is relatively advanced,—namely those with $n+2$, $n+1$ or n phases, which, according to a very fortunately chosen nomenclature of Trevor, he terms nonvariant, monovariant and divariant systems, a terminology which I gladly endorse. In my opinion the simultaneous treatment of the quantitative side would have afforded decided advantages. In any event I should have desired to see given the thermodynamic derivation of the phase rule; whereby at the same time opportunity would have arisen to introduce the graphical treatment of van Rijn van Alkemade, and whereby a theoretical basis would have appeared for the Theorem of Le Chatelier,—which is chosen as a second principle.

The very recent extension which our knowledge of the systems of three components has received at the hands of Schreinemakers shows sufficiently how entirely necessary is the graphical potential method for the solution of the yet unsolved problems. For the reason that the author has omitted this method, his exposition of the phenomena in systems of three components is much less satisfying than is the case with the simpler systems. I would also, for the systems with three components, have made more use of Schreinemakers's graphical deductions from the isotherms for clear exposition of the very complicated relations obtaining upon them. Yet even in this section of the book one finds much that is excellent, and the author has succeeded satisfactorily in his classification of this difficult material.

A chapter on Constituents and Components presents a thorough and original discussion of the question regarding the selection of the number of components, and the book closes with a brief statement of the little that is known concerning systems of four components. Criticism of details would here be out of place; he who studies the book so thoroughly as to penetrate to the details will have developed sufficient judgment to put a question mark here and there, or to draw some different conclusion. The comprehensiveness of the work deserves all praise; I have found in it more than one fact that was unknown to me, and of the important phenomena which might have found a place I miss only the dissociation phenomena *par excellence* (calcium carbonate and the like) and the ternary alloys.

I have only *one* serious objection, namely to the idea of the author that in a liquid phase of two components one of them is to be regarded as solvent and the other as dissolved substance. This view plays a rather prominent part in the book. The author derives from it a distinction between fusion curves and solubility curves and so separates phenomena which I prefer to regard as wholly similar. His view bears upon the interpretation of the point of miscibility of two liquid phases and, further, of many equilibria in systems of three components. I have not been able to find any more secure experimental basis for this pregnant idea than the solubility curve which Bathrick is said to have found for sodium chlorid in mixtures of alcohol and water. These experiments I can not accept as decisive, and this for the reason that the conclusions based upon them would in my opinion denote a step backward. They conflict absolutely with the hardly won insight into the gradual variation of the properties of a liquid mixture of two components when the ratio of these components is gradually varied. I especially regret the assumption of this standpoint in a book which seems destined to exert a powerful impulse upon the spread of knowledge concerning heterogeneous equilibria, and of which I hope that it will introduce a new phase in the development of the chemistry of the phase rule. *H. W. Bakhuis Roozeboom*

The Principles of Mathematical Chemistry. *Georg Helm. Authorized translation by J. L. R. Morgan. 12mo, viii and 228 pages. John Wiley and Sons; New York, 1897. Price $1.50.* Helm's

Mathematische Chemie was one of the earliest of the series of thermodynamic works which is still coming into existence as a result of the extensive chemical applications of thermodynamics during the last ten years, and it has a peculiar interest as being an attempt to present in orderly arrangement a discipline which shall be for chemistry what mathematical physics is for physics. Its arrangement includes the energy law, with particular applications to chemical phenomena; the entropy law, with applications to physical changes of state; Gibbs's potential theory, with applications to dissociation, solution theory and the velocities of reactions; and, finally, the phase rule. The book, as a monograph, is interesting and has many strong points,—notably in its application of the energy principle, its analytical treatment and graphical representation of dissociation isotherms, a deduction of the partial differential equations involving entropy, volume, potential, temperature, pressure and the masses of components, a judicious choice of material, and a fairly rigorous and uniform mathematical style. The reviewer prefers a different arrangement, based upon the phase rule,—which can be made far more logical and coherent than that adopted by Helm,—and he fails to find in Helm's book a satisfactory justification for either of the two great thermodynamic principles or for the Gibbsian criteria of equilibrium. The treatment of the absolute thermometric scale is also an unsatisfactory important feature, and marginal references to the original literature of the subject are sorely missed. For such reasons the author's original little work is a good monograph but a poor text book.

Mr Morgan's English version has been read by Helm. It is intelligible enough, but can scarcely be called a close translation. A careful reader, too, does not like such things as the statement (page 34) that a substance is completely «combusted», reference (preface) to «the presence of experiments in this book» for *die Bezugnahme auf Experimente*, and (page 41) «the ways of the energy of volume» for *das Wesen der Volumenergie*; the manner in which the translator has often failed to reproduce what his author says is illustrated by the remainder of this last passage. And the publishers have offended the eye by printing a ∂ which does not line with the letters with which it is set. Still, notwithstanding these objections to details, the book before us is an important one and can not fail to be of service to students of scientific chemistry.

J. E. Trevor

An Outline of the Theory of Solution and its Results. *J. L. R. Morgan. Small octavo, 63 pages. John Wiley and Sons; New York, 1897. Price $1.00.* To present an elementary exposition of the theory of solutions is announced to be the purpose of this little book. It considers successively the Theory of Solution, Methods for the Determination of Electrolytic Dissociation, The Theory of the Voltaic Cell, and Analytical Chemistry from the Standpoint of Electrolytic Dissociation; doing this in four chapters which seem to be largely a condensation of the treatment in Ostwald's *Lehrbuch* and *Grundlagen* and Le Blanc's *Elektrochemie.* The author's idea is a useful one and he has assembled much interesting material in simple form, but the actual exposition is far more rudimentary than «elementary». On page 2 he states «All gases . . . contain in unit volume the same number of molecules», and lets the matter go at that. On the next page he «unites» the analytical expressions

$$v = v_0(1 + \alpha t)$$
$$p = p_0(1 + \alpha t)$$

to obtain

$$pv = p_0v_0(1 + \alpha t),$$

while, as thus presented, they give

$$pv = p_0v_0(1 + \alpha t)^2,$$

which is of course wrong; the matter is not clearly stated. On page 7 ammonia is supposed added to dissociated ammonium chlorid «until all the HCl is used up», which is unfortunate as an illustration. Two pages later the osmotic pressure is stated to be due to «the tendency of the molecules to get out of the space», which leads to some absurd remarks upon page 11. The Ostwald-Nernst influence experiment is cited to prove that ions are charged with electricity (page 19); the reader is led to believe that Ostwald's dilution-formula holds for sodium chlorid and like salts (page 22): and «indifferent ions» are asserted to have no effect upon solubility equilibria, in spite of all common experience to the contrary (page 23).

The present writer recognizes little as familar in the description, on page 34, of his work upon the inversion of sugar by acid salts; it is asserted (page 46) that Bancroft's oxidation and reduction cells require «of course» a siphon connection between the two liquids,—which is entirely incorrect, most of Bancroft's measurements having been made in fact with a mercury connection. Further, in order to account for the charge assumed by a metal in a salt solution we are told that «All neutral substances are charged with electricity . . . so if we remove the positive, the negative remains behind»; and there appears on page 57 the assertion that the ions in the reactions of qualitative analysis are related through Ostwald's dilution-law, which is of course not true. Many more such objections could be made.

In a different category of faults lie the statements that «molecules of sodium chlorid go into solution» (page 21) where ‹sodium chlorid goes into solution› is meant; a confusion of ‹electricity› with ‹electrical energy›, on page 36; the incorrect translation of *Wanderung* by ‹wandering›; and the consistent spelling «Helmholst» wherever Helmholtz's name appears.

If any justification or physical meaning were given to the important formulas on pages 22, 37 and 41 the book would afford a fairly satisfactory outline of certain current views, but as it is, the whole presentation must be characterized as superficial,—it will certainly not, as is claimed in the preface, enable its reader to follow the current literature of the subject. *J. E. Trevor*

Introductory Course in Differential Equations. *D. A. Murray. Crown octavo, xv and 234 pages. Longmans, Green and Co. New York, 1897. Price $1.90.* The present work is a text book designed to supply an introductory acquaintance with the solving of differential equations; it is considerably smaller than any similar work with which the present writer is acquainted, and is accordingly intended to be a chapter supplementary to any brief course in integral calculus. We find in it a systematic arrangement which includes—under Equations involving two Variables—equations of the first order, linear equations and equations of the second order; followed by both ordinary and partial differential equations involving more than two variables. The volume is concluded by a chapter of miscellaneous notes to serve those who will continue the subject farther than it is carried in the book. The text is clearly and concisely written, many of its illustrative examples are taken from mechanics and physics, and it is enlivened by very interesting historical and biographical notes relating to the development of the special topics treated. Many beginners will find a Short Course of selected articles, arranged by the author, admirably adapted for self-instruction in the rudiments of the subject. The mechanical get-up of the book is good; the use of a long primer ∂ in brevier footnotes and examples, where it does not line with the other letters, is however a carelessness which the publishers should not allow to occur again.

J. E. Trevor

Chaleur et Énergie. *E. Ariès. Small octavo, 167 pages. Gauthier-Villars et Fils; Paris. Price 2.50 francs, in boards 3 francs.* We have here a presentation of the subject matter usually found in works on thermodynamics, but broken into two distinct parts,—the first advancing such theorems as can be maintained concerning only the quantities of heat which enter into thermodynamic changes, while the second includes those theorems which must be added when the concomitant development or absorption of work is also considered. This procedure is regarded by the author as introducing a very desirable simplification into the exposition of the theory of heat, and it may be said that he has done the thing in a clever manner. M. Léauté, the director of the *Encyclopédie scientifique des Aide-mémoire* in which series the volume appears, has been so impressed by the book as to introduce it by a preface written by himself. The closing chapter is devoted to a systematic account of the theory of the characteristic functions introduced by Massieu. The book is printed upon heavy paper, which is so tough and translucent as to remind one of parchment.

J. E. Trevor

Die Chemie im täglichen Leben. *Dr. Lassar-Cohn. Second, revised and enlarged edition. vii and 303 pages. L. Voss; Hamburg, 1897. Price, bound, 4 marks.* Lassar-Cohn belongs evidently to the small class of men who have pronounced talent for making popular addresses. Twelve lectures upon chemistry in its immediate bearing upon the arts are assembled in the present volume. They were originally given before popular assemblies in the university town of Königsberg. In them is presented in a clear, flowing and fascinating manner a lot of well ordered scientific information about combustion, food-stuffs, liquors, explosives, tanning, bleaching, dyes, paints, alkalies, glass, soap, photography, metals, alloys and drugs. A popular treatment of many of these things is a right difficult matter, but our author has picked his way through them in such wise that an ordinary audience can readily follow. The lectures are so planned that each can be read in an hour; they can be warmly recommended to all who are interested in what science can tell about common things.

J. E. Trevor

Ueber den Urstoff und seine Energie. *H. Keller. 58 pages, Teubner; Leipzig, 1896. Price 2 marks.* With a great parade of mathematical symbolism this book defends a view that bodies are composed of atoms, which are composed of like primitive atoms, which are mutually attracted according to Newton's law; that the attraction of atoms for the primitive atoms maintains the latter in vibrations which constitute heat, and that the ether is primitive substance not yet condensed to primitive atoms.

J. E. Trevor

Das Interferenzprinzip. *Dr. Hallervorden. Stuber, Würzburg. 30 Pf.* A perfectly unintelligible brochure, advancing the thesis that: All natural laws are special cases of interference. The author complains that publication had been refused by Ostwald.

J. E. Trevor

The Elements of Physics. *E. L. Nichols and W. S. Franklin. Volume III, Light and Sound. viii and 201 pages. The Macmillan Co. New York, 1897. Price $1.50.* Nichols and Franklin's Elements of Physics has already received mention in this Journal, **1**, 104 and 181, upon the appearance of the first and second volumes of the series; the concluding third volume, on Light and Sound, is now out. The character of the work,—that of a clear theoretical treatment of the more prominent features of the subject, using calculus methods wherever desirable and omitting descriptions of experiments,—is maintained. The choice of topics is admirable throughout and the treatment is concise, logical and clear, so that the book as a whole is very instructive and can not fail to be an important contribution to the literature of elementary physics. This volume has a convenient size, it is well printed, and, like its two predecessors, is profusely illustrated by simple and well chosen diagrams, curves and schematic drawings of apparatus. *J. E. Trevor*

The Outlines of Physics. *E. L. Nichols. 12mo. xi and 452 pages. The Macmillan Co. New York, 1897. Price $1.40.* The avowed purpose of this book is to outline a short course of physics which shall be an equivalent of the one year's work in «advanced» mathematics now required for entrance to many American colleges. The usual topics of mechanics, heat, electricity, magnetism, sound and light are presented, with a wise selection of material and accompanied by extensive descriptions of illustrative experiments. The course of experimentation so offered is admirably adapted to the purposes of rudimentary instruction, and it so constitutes by far the best feature of the book. In the remainder of the text the reviewer is grieved to note the frequent appearance of dogmatic statements, especially with regard to the mechanistic conception of natural phenomena. Examples of these are:—«Friction, adhesion . . . and many kindred phenomena are due to forces, the sphere of action of which is very small, comparable indeed in size to the distances which separate the molecules of the solid or liquid» (page 86), «Heat is the name given to the form of energy due to some motion of the particles of a body among themseleves, and not of the body as a whole» (page 148); «Rise of temperature is always an indication that work is being done» (page 161).

It may, however, be said that because the system of simple physical experiments here given will furnish an admirable basis for instruction in physics in the fitting schools the teachers in charge of such work can refer to the volume with great profit in arranging the practical side of their courses. Such experiments, arranged with the suitably shortened text of such a book as Mach's *Leitfaden der Physik* would furnish an almost ideal text book for our preparatory schools. The present volume is well printed and is especially well illustrated. *J. E. Trevor*

The Tutorial Chemistry. *Part I. Non-Metals. G. H. Bailey; Edited by W. Briggs. 16mo. viii and 226 pages. Hinds and Noble; New York, 1897. Price 3s. 6d.* This is the first part of an elementary text book of chemistry. After a short general introduction the author treats of hydrogen and the haloid acids, the physical properties of gases, the compounds of hydrogen with oxygen and with sulfur, the halogens, oxygen, sulfur, nitrogen, phosphorus, carbon, silicon and boron, and concludes with a rather inadequate chapter of chemical problems. Part II, in preparation, is to treat of the metals and «Chemical Physics». The book unfortunately has directions for experiments interspersed throughout the text instead of having them collected into a suitable manual for laboratory use, and in these directions the student is told just what he should see, so that he loses the training of finding out for himself what happens. The Atomic Theory is prominent in the theoretical part. The following quotation shows the kind of statements there made. «The molecular weight of any gas is equal to the density of the gas (in relation to hydrogen) multiplied by 2. This definition of molecular weight depends on the acceptance—(1) Of the assumption that the hydrogen molecule consists of two atoms, (2) Of Avogadro's hypothesis». Aside from these faults, which are altogether too common in books of this class, the book is up to date. Argon and helium are mentioned, the material for treatment has been carefully selected, and for the most part the statements are clear and concise. Two errors which deserve attention are the giving of the combining weight of oxygen as 15.96 and the statement that cryohydrates are compounds.

F. L. Kortright

Theorie und Praxis der analytischen Elektrolyse der Metalle. *Bernhard Neumann. Large octavo, viii and 224 pages. W. Knapp. Halle, 1897. Price 7 marks.* The first thirty pages are taken up with a discussion of the theory of electrolysis, condensed directly from Ostwald. Then follow chapters on the sources of current, battery, thermopile, accumulator and dynamo; on measurements of current and difference of potential; on way of regulating the current and on the general arrangement of an electrochemical laboratory. The remaining hundred and twenty pages are devoted to the details of electrolysis. This part of the book differs from all previous works on the same subject in that the current is not measured in cubic centimeters of gas per minute and that the electromotive force is recognized as an important feature, especially in the separation of two metals. These two points should be sufficient to gain for the book a place in all laboratories—at any rate, until others follow along the same line. *Wilder D. Bancroft*

Quantitative Analyse durch Elektrolyse. *A. Classen. Fourth Edition. Octavo, viii and 249 pages. Julius Springer; Berlin, 1897. Price 8 marks.* The fourth edition differs essentially from the preceding three. The gas voltameter is discarded and we now have exact data in regard to the electromotive force and the current density at the cathode. While the current density is the important factor, it is not measured directly and it would have been well to have given also the actual strength of the current passing through the electrolytic cell, especially since the actual surface of the cathode is nowhere given and there is nothing in the book to show how this is to be determined. The other improvements in the book are the recognition of the importance of the electromotive force as a factor in the separation of metals, and a theoretical introduction compiled with the assistance of W. Löb. The reviewer would call attention to the excellent paragraph on the significance of the current density, while the next section on the question of the resistance would be fully as good if it were a little more complete. On the other hand the definition of an ampere, page 12, as the strength of current which will precipitate 0.328 mg copper per second is not suitable for a student. It is very much to be regretted that some twenty pages of the introduction should have been given up to a bitter attack upon Rüdorff.

To many the description of the arrangement of the laboratory at Aachen will be very welcome and it is not too much to say that this latest edition of a standard work is vastly superior to the preceding editions and will do much towards introducing more rational conceptions among the students of electrochemistry.

Wilder D. Bancroft

Entwickelung, Bau und Betrieb der elektrischen Oefen. *W. Borchers. Small octavo, 65 pages. W. Knapp; Halle, 1897. Price 3 marks.* This is the ninth volume of the electrochemical encyclopaedia published by Knapp and is a reprint in book form of articles which have appeared in the Zeitschrift für Elektrochemie. Since the articles have already been reviewed in this Journal, **1**, 391 (1897) it is only necessary here to call attention to the republication in a convenient, compact form. *Wilder D. Bancroft*

Pouvoir calorifique des Combustibles, solides, liquides et gazeux. *M. Scheurer-Kestner. 16mo, xiv and 287 pages. G. Masson; Paris, 1896. Price 5 francs.* The second half of the book is purely technical, dealing with the heating effects of different combustibles and methods of determining the same. The first part of the book is devoted to a discussion of the different types of calorimeters which have been devised and to details in regard to thermometers. The author does not consider the Beckmann thermometer an improvement over the one devised by Walferdin and is rather indignant that Beckmann's name should be associated with any thermometer. In a series of thirteen appendices are given some numerical data for the benefit of the technical chemist. *Wilder D. Bancroft*

Electromoteurs et leurs Applications. *G. Dumont. Small octavo. 183 pages. Gauthier-Villars et Fils; Paris, 1897. Price 2.50 francs, in boards 3.00 francs.* This is one of the volumes of the *Encyclopédie des Aide-Mémoire.* Under electric motors with continuous current we have chapters on the different types; on the results of changes in coupling; on the best conditions for running motors and a brief sketch of the compound motor. Under electric motors with alternating currents we have a discussion of the different types; of monophase and polyphase motors and a comparison of motors with stationary and rotating fields. The remaining forty pages are devoted to a consideration of electrical transmission and its merits; of the power necessary for certain specified mechanical operations and of the various applications of electric motors. The author has been distinctly successful in the way he has developed the subject.

Wilder D. Bancroft

L' Acétylene. *Raoul Pictet. Octavo, 187 pages. Georg et Cie; Geneva, 1896.* This volume is intended to increase the general knowledge in regard to acetylene and to advertise the Pictet patents. Of special interest are the remarks on the impurities in the gas, the methods of removing them and the temperature reached by the combustion of acetylene. There seems to be no experimental justification for the statement that this temperature is above 4000°.

Wilder D. Bancroft

Le Carbite. *Raoul Pictet. Octavo, 75 pages. Georg et Cie; Geneva. 1896. Price 1.50 francs.* After a brief discussion of the present methods of preparing calcium carbid, the author points out the foolishness, as it seems to him, of obtaining all the heat necessary for the reaction at the expense of electrical energy. He then describes a patent of his own for raising the temperature in three stages by means of coal, the oxyhydrogen flame and the electric arc. He estimates that this process will reduce the price of carbid in France from 200 to 82 francs per ton. *Wilder D. Bancroft*

Loi des Equivalents et Théorie nouvelle de la Chimie. *G. Marqfoy. Large Octavo, xxxii and 500 pages. Masson et Cie. Paris, 1897. Price 7.50 francs.* «There are theoretically in nature as many simple molecules as there are prime numbers in the indefinite series of integers beginning with unity.» «There are practically in nature as many simple molecules as the Creator has deemed necessary to select from the indefinite series of prime numbers for the purpose of the Creation.» «In the beginning there was only hydrogen. In the course of time, the movements of hydrogen having followed a certain law favorable to the formation of oxygen, that is to the creation of a molecule containing two atoms, the molecule was produced on a large scale. Oxygen was formed and appeared in the Universe.» «After these two simple bodies, hydrogen and oxygen, were formed, their union gave water. I note in these phenomena a striking analogy to the magnificent description in Genesis.»

Wilder D. Bancroft

Das mikroskopische Gefüge der Metalle und Legierungen. *H. Behrens. Octavo, viii and 170 pages. L. Voss; Hamburg, 1894.* Though this book is not a new one, it is worthy of a great deal more attention than it has yet received—both for what is and for what is not in it. The author describes in detail the methods which one would employ in studying metals and alloys under the microscope and then gives the results of his own investigations, adding sixteen handsome plates which should be of great benefit to the student. We find in the book the signs that characterize a new subject. The methods have not yet yielded a tithe of the results which will some day be forthcoming. The study of the microscopical structure of alloys ought to be of the greatest assistance in determining what solid phases can exist in equilibrium with the molten metals. So far this is not the case. It is impossible, from any of the data given, to draw trustworthy conclusions save in the most exceptional cases. This is in part due to the stress laid upon the form of the crystalline network; but chiefly to the fact that the subject has not been studied, keeping in mind the freezing point curves and the conclusions to be drawn from them by an application of the Phase Rule. There is here a most interesting field of research and this book of Behrens is of great value as pointing out what is to be done and how to do it. *Wilder D. Bancroft*

Encyclopädie der Elektrochemie. VIII. Unsere Kentnisse in der Elektrolyse und Elektrosynthese organischer Verbindungen. *Walther Löb. Small Octavo, 42 pages. W. Knapp; Halle, 1896. Price 2 marks.* This little book gives a very satisfactory summary of what little has yet been done in the way of organic synthesis by means of electrolysis. The classification is based on the chemical nature of the substances electrolyzed and not on the nature of the reaction, this form of treatment being made necessary by the very incomplete development of the subject. The author makes the subdivisions: fatty alcohols, ketones and acids; aromatic alcohols, acids, amins and nitro-compounds; alkaloids, blood and albumen. The last few pages are devoted to electrolysis with alternating currents. *Wilder D. Bancroft*

Vorlesungen ueber Thermodynamik. *M. Planck. Large 8vo, vii and 248 pages. Veit und Comp. Leipzig, 1897.* Planck, ever since the publication in 1887 of his papers on the principle of the increase of entropy, has been a prominent figure in the field of thermodynamics and his lectures upon this subject at the University of Berlin have attracted considerable attention. In editing these lectures for publication he has supplied us with a uniform and connected exposition of thermodynamics, whose chief characteristic lies in asserting the principle of the spontaneous increase of entropy in natural processes to be the most general formulation of the second law. The result hereby attained is a uniform treatment from a definite standpoint, and not a broad account of the present state of development of thermodynamic science, which accounts for the absence from the book of all citations of the original literature of the subject beyond an appended bibliography of Planck's own writings in this field.

In the distribution of his material the author has devoted half the book to general theory and the remainder to applications. The first half treats the first and second laws of thermodynamics, with prefatory consideration of the ideas of temperature, of molecular weight and of quantities of heat. The initial remarks upon thermometry are good, a section (§ 31) upon possible critical points for fusion equilibria is very pleasing, and the sections 34 to 38 upon molecular and combining weights are altogether excellent. The author arrives at the two laws of thermodynamics through exclusion of the two types of perpetual motion, according to the method adopted in his earlier publications. As was to have been expected he attacks, whenever possible, the principles of the recent doctrine of energetics. In the latter half of the book we find extended applications of the general theory to one-component systems, to polycomponent systems and to the special cases of chemical equilibrium in gases and in dilute solutions; this matter is largely an elaboration of the familiar exposition in the author's papers of 1887. An interesting feature is the adoption of the notation Q for infinitesimal quantities of heat, to avoid all possibility of misconceiving dQ or $d'Q$ (see this Journal 1, 56) as the differential of a finite quantity.

The book as a whole is interesting and instructive and will doubtless find many readers. A beginner however would probably do well to study the subject historically—in order to gain a broad view of it—before taking up so specialized a work; especially, too, since some things, such as the thermodynamic surfaces, do not appear in it at all and others, such as the Gibbsian potential theory, are presented from but a single point of view. Lack of historical perspective may be excused in a monograph, which the present work really is, but in an introductory treatment of thermodynamics the case is otherwise. *J. E. Trevor*

Zeitschrift für comprimirte und flüssige Gase. *Issued by M. Altschul. Monthly, price 4 marks per quarter.* A very interesting addition to the periodical literature of physics is the new *Zeitschrift für comprimirte und flüssige Gase*, edited by M. Altschul and published by L. Estermann, Alderstr. 14, both of Berlin. The enterprising young editor is already well known for his researches on critical points and on the properties of bodies at low temperatures, and he has enlisted for his Journal the support of apparently all the prominent investigators in this special field. His *Zeitschrift* is intended to supply a natural place of publication for papers which would otherwise be scattered through the scientific literature, and at the same time to make the results of special research more readily accessible to technical circles than has hitherto been possible. All study of the behavior of bodies at low temperatures and under high pressures has direct bearing upon physical chemistry, so all such results which appear in the new publication will be regularly reviewed in this Journal as they come out. The two numbers already issued contain articles by Pictet, Wiebe, Altschul, Thilo and Thiesen, together with scientific and technical notes and reviews of books. *J. E. Trevor*

Kurzes Lehrbuch der chemischen Technologie. *Ludwig Medicus. Large Octavo, xiii and 1170 pages. H Laupp; Tübingen, 1897. Price 24 marks.* Professor Medicus's ‹Technology› gives one the impression of a most successful attempt to compress within the space of one volume, though a large one, a fairly full account of all the numerous manufactures—from pottery to aniline dyes—that come under the supervision of the technical chemist. Although, as is necessary in a book which undertakes to give a view of so wide a field, the student is continually referred to special works for the more minute details, none of the more important processes appear to have been omitted ; and the author has evidently endeavored to indicate the lines on which progress may be expected in the immediate future, by inserting short notices of the newest suggestions and improvements—in some cases even when they have not been as yet carried out in practice. The recent applications of electricity have also received suitable prominence.

The work begins with 130 pages on heating, lighting, water, ice production, air and gases, after which follow metallurgy and inorganic industries (pp 131-590) and the organic industries (pp 591-1145). The reader is expected to have the training of the average chemist, nothing more, the ice machine is treated of without reference to thermodynamical theory, electrometallurgy is dealt with as far as possible without illustrative calculations, and the chapter on organic dyestuffs contain much that the ‹average› *organic* chemist might very well be expected to be familiar with—but though, in one sense, the work is intended primarily for the beginner, yet the carefully written descriptions and comparisons of the various processes, and the numerous illustrations throughout the book make it most interesting reading for all who wish to obtain an idea of the interrelation of the various chemical industries and of their growth and present position. *W. Lash Miller*

Traité de Chimie organique appliquée. *A. Joannis. Two volumes, 688 and 718 pages respectively. Gauthier-Villars et Fils; Paris, 1896.* This book is apparently intended for readers with no previous knowledge of organic chemistry. It begins with an introduction of ninety-five pages containing paragraphs on Gay Lussac's law, molecular and atomic weights, valency, etc., etc.; also on organic analysis and on the determination of molecular weights by vapor density measurements and by measurements of the boiling points, freezing points or vapor tensions of solutions. It is a little surprising to find that Beckmann's name and his convenient modifications of the boiling point apparatus have been omitted; and to read—so many years after v. Baeyer's work on the subject—that the prism formula is the only one that correctly expresses the constitutional formula of benzene!

The remainder of the work is divided into sixteen chapters—on hydrocarbons, on alcohols, on phenols, etc., etc—each of which is subdivided under the headings ‹*Généralités,*› ‹*Étude particulière*› and ‹*Applications*›; so that the pages devoted to ‹applied organic chemistry› in the stricter sense form but a small fraction of the whole. Under the latter head special attention is paid to analytical methods: for example, under ‹sugar› are detailed instructions for examining beets, animal charcoal and residual pulp; for estimating reducing sugars, saccharose, ash and water; for determining alkalinity during the process of manufacture and for calculating the probable yield on refining—so that the work may serve not only as a book of instruction for the student but to a certain extent as a handbook for the technical chemist. *W. Lash Miller*

Grundzüge einer thermodynamischen Theorie elektrochemischer Kräfte. *Alfred H. Bucherer. Small octavo, 144 pages. Craz und Gerlach; Freiberg i. S., 1897. Price 4 marks.* «It was the absence of satisfaction which I felt on thorough study of the modern theories of electrolytic solutions and electrochemical forces as upheld chiefly by Arrhenius, Ostwald and Nernst, that induced me to compare the consequences of these modern views with those of thermodynamics. . . . When such molecular structures as the ions are credited with an independent existence, they are *ipso facto* removed from the realm of chemistry. . . Not to mention other insufficiencies, the attempt made by Nernst to express the potential difference in a cell as a function of osmotic pressure and ‹solution-tension› (a conception introduced by Nernst himself) must be considered as signally unsuccessful. In the interest of science, I have judged it the more necessary to attach great importance to a thorough and detailed proof of this want of success, as Ostwald, in his widely read *Lehrbuch der chemischen Energie* has endeavored to erect on Nernst's foundations a complete theory of electrochemistry.»

These sentences from the preface are sufficient to characterize the author's standpoint with reference to the ‹Arrhenius-Ostwald-Nernst› theory. The reader is accordingly not surprised to find the time-honored objections to the ‹existence› of ions set out *in extenso*, though he may, perhaps, find it a little hard to consider the above mentioned chemists responsible for all the consequences derivable from our author's conclusion that «in order to be consistent, Nernst and Ostwald must assume that in the case of pure water, free from air, the vapor tensions of the hydroxyl ions and hydrogen ions in the vapor over the water must be equal to those in the water itself.» Not to mention the difficulty attaching to the author's conception of the ‹vapor tension of hydroxyl ions in the water itself›, is it not rather aggressive to attempt to fasten such a monstrosity on the ‹A-O-N› theory with no other excuse than that «according to correct energetics, the gaseous phase of a substance is completely equivalent to the liquid, merely because it is in equilibrium with the latter»?

As depicted by Bucherer, the modern electrochemical theories are certainly much in need of improvement ; but the task is not so easy as our author evidently conceives it to be, and at the very first step he falls into a nine year old trap. «E. Wiedemann ascribes the abnormal depression of the freezing point, in the case of electrolytes, to an influence exercised by the dissolved substances on the degree of polymerisation of the molecules of the solvent. On dissolving an electrolyte, the solvent becomes more polymerized, hence in the equation—

$$\textit{Depression}\ (=D) = \textit{Const} \times \frac{\textit{No. molecules dissolved} = n_1}{\textit{No. molecules solvent} = n}$$

n is lessened, and the depression has a greater value»—All the arguments in favor of dissociation into ions which are derived from the abnormal freezing-points of electrolytic solutions thus go by the board: the salt is not dissociated, but the solvent is polymerized!

Unfortunately for all this and for the theory of solutions which the author builds up on this foundation, Wiedemann's ‹explanation› was based on a want of familiarity with the formula under discussion. The expression for D just given is *not* a consequence of the ‹modern theory of solution› at all, it is an empirical formula set up by Raoult, and the ‹theoretical› formula

$$D = \frac{2n_1T^2}{wL}$$

does not involve n! [T is fusion temperature, w the mass of solvent and L its heat of fusion]. As is well known experiment has decided in favor of the second expression. It is true that in the

‹ theoretical › formula for alterations in the vapor tension of a solvent on addition of a salt, the quotient n_1/n does occur, but in this case (as those are aware who understand the derivations of the formulae they employ) n refers to the solvent *in the form of vapor, not in the solution.*

After this inspection of the foundations of the author's theory of solutions, and of the argument which he relies on to do away with the ions, it will be sufficient to pass quickly over the remainder of the work. One striking peculiarity however deserves a moment's notice. In the preface we read « By extensive use of the vapor tensions of the metals, I believe that I have rendered useful for the science of electrochemistry a physical quantity previously kept unduly in the background.» And accordingly the text and formulae bristle with references to the vapor tensions—at ordinary temperatures—of lead, copper, zinc and iron, magnetic and nonmagnetic.

The author himself concedes that these hitherto neglected quantities are « hardly to be determined experimentally » but seems not to see how unpractical it is to « teach the reader how to carry out the necessary calculations » by a method whose results are confessedly inaccessible to quantitative interpretation.

In this connection perhaps one more quotation may be allowed: « In passing judgment on Nernst's theory [Nernst's only ?] this question must be answered first and foremost, viz: – to what extent does the theory allow us to express the E.M.F. in terms of *well known directly measurable* physical quantities ? » — for example, the tension of the vapor of *lead* given off at 15°C by an aqueous solution of lead chlorid !

The object avowed by the author of the work under review, viz: – to subject the modern electrochemical theories to a searching criticism in the light of the facts, is certainly a worthy one; to carry out such a design successfully, however, is possible only to one who is thoroughly familiar with the theories in question, with thermodynamics and with the literature. *W. Lash Miller*

REVIEWS

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

General

On the Combustion of Coal Gas in Motors. *F. Haber and A. Weber. Ber. chem. Ges. Berlin.* **30**, *145* (*1897*). Two motors of different types were experimented on, viz:—(A) in which the gas inlet was either completely open or completely closed; if working with less than the maximum load the number of explosions was less than the number of strokes of the piston; and (B) in which an explosion accompanied each stroke, but the aperture of the gas inlet, and consequently the percentage of coal gas in the explosion cylinder varied with the load. When the motors were doing full work no noticeable amount of the coal gas escaped combustion. With small loads, on the other hand, the loss rose as high as eight percent; the authors refer this to the formation of non-explosive or slowly explosive mixture of gas and air, and discuss the mechanism of the formation of such mixtures in motors of the type (A). *W. L. M.*

The Chemical Proportions. *F. Wald. Zeit. phys. Chem.* **22**, *253* (*1897*). After a paragraph on the subject of chemical identity and chemical difference, the author undertakes to show that substances with the properties generally ascribed to ‹pure chemical compounds› (among which is the ability to take part in ‹chemical reactions›) must necessarily be subject to certain restrictions as to their composition. A further development leads him to the laws of combination in reciprocal and multiple proportions, which, he asserts, are therefore contained implicitly in the very definition of chemical compounds and reactions. As the ‹laws of proportion› form the basis of the present atomic theory the subject is of the first importance. [Wald makes the assumption that, if we have a compound A_nB, the compounds $A_{n-x}B$ are «possible» where x is an integer having any value between n and unity. While this may be true, the burden of proof is upon the author to show that it is so. Until this is done, this remarkable paper will hardly receive the attention which it deserves. Eds.] *W. L. M.*

Lability and Energy in Relation to Protoplasm. *Oscar Loew. Reprinted from the Bull. Coll. Agriculture, University of Japan.* **2**, *No. 7, 393.*

Lability. «Labile (kineto-labile) compounds, which readily change into an isomeric stable modification, contain certain atoms loosely bound, which condition is caused by a certain amount of kinetic chemical energy counteracting the force of affinity existing between the atoms of the compound. Every energy of the kinetic kind is motion, and motion can be conveyed from one body to another.»

Energy. «I have adopted the definitions of *Grant Allen*: ‹Chemical *affinity* is the force that aggregates atoms, chemical *energy* is motion which separates atoms and resists the aggregation of atoms. Force and energy, the aggregative and the separative powers, are incessantly opposing and antagonizing one another in all bodies, great or small› . . . *Substances that very easily enter into reactions can hold their components only loosely bound*, and the force of affinity is here counteracted by *chemical energy*.»

Protoplasm. «How, then, can the lability of aldehydes be explained by a continuous atomic motion? . . . Both the hydrogen atom and the oxygen atom are continuously in a fierce state of vibration. . . Such a state of kinetic chemical energy was foreseen by me to exist in the active albumin, which I consider a product of the condensation of the di-aldehyde of aspartic acid. . . I have explained in former Bulletins that physiological phenomena compel us to infer the existence of a *labile* (active) and a *stable* (passive) modification of albumin, and that the former alone is capable of leading by ‹organization› to living protoplasm.»

W. L. M.

The «Unit» of the Atomic Weights. *F. Küster. Zeit. anorg. Chem.* **14**, *251* (*1897*). A reply to Seubert in which the author points out that other ratios have been determined with more accuracy than that of oxygen to hydrogen and that therefore there is no reason for not keeping O = 16 as the normal. He also makes the excellent suggestion that densities should be referred to one-sixteenth of the combining weight of oxygen instead of to air as unity. *W. D. B.*

The Basis of the Atomic Weights. *B. Brauner. Zeit. anorg. Chem.* **14**, *256* (*1897*). An elaborate argument in favor of keeping O = 16 instead of H = 1. The point of view is so thoroughly rational that few will find fault with it. *W. D. B.*

Fourth Annual Report of the Committee on Atomic Weights. Results published in 1896. *F. W. Clarke. Jour. Am. Chem. Soc.* **19**, *359* (*1897*.) The usual complete statement of the work done in this field during the preceding year. The author recognizes that many people consider atomic weight determination as not worth the time spent upon them and he attempts to meet this objection by citing the case of a Baltimore firm which determines the chromium in chrome iron ore using 52.1 as the reacting weight of chromium while a Glasgow firm uses 52.5 as the proper value. The author overlooks three points in this argument. 1. The discrepancy is in this case nearly one percent, so that this is not one of the instances objected to. 2. The matter is purely a technical question and not a scientific one. 3. If the Baltimore firm knows the data used by the Glasgow firm, there is no more hardship than if one were to estimate chromium in kilograms in one place and in pounds in the other. Even if we grant the author's premises and conclusions, he has only proved that the people who do atomic weight determinations have worked upon the wrong substances and have therefore not spent their time to the best advantage. *W. D. B.*

Latest Science. *J. E. Harvey.* (*Brochure*). A string of annotated quotations, from many scientific publications, intended to indicate a «common mechanical cause of chemical potential and atomic spectral lines.» *J. E. T.*

Calculation of Heats of Dissociation and Formation by Means of a Hypothesis in regard to Valence and Affinity. *J. Sperber. Zeit. anorg. Chem.* **14**, *164* (*1897*). Extracted from the author's book, the Parallelogram of Forces, reviewed in this Journal **1**, 108 (1896). *W. D. B.*

Certain Changes in the Beckmann Apparatus. *W. Meyerhoffer. Zeit. phys. Chem.* **22**, *619* (*1897*). The improvements consist in a Witt stirrer which surrounds the thermometer and in having a water cooler around the tube containing the crystals. The solution is heated in an air bath. *W. D. B.*

On a Specific Gravity Bottle for Liquids. *F. Campanile. Nuovo Cimento*, (*4*) **5**, *183* (*1897*). It was noticed that the position of the stopper affected the readings with the usual apparatus and the author has therefore invented a bottle with a stopcock. The capillary side tube can be closed with a stopper or a stopcock as seems preferable. *W. D. B.*

Biological Thermodynamics. *A. Chauveau. Comptes rendus*, **124**, *540*, *596* (*1897*). Two papers on «internal work» in the muscles. *W. D. B.*

Monovariant Systems

The Heats of Vaporization of Liquids. *S. R. Milner. Phil. Mag.* [*5*] **43**, *291* (*1897*). At the surface of a liquid one may assume an excess of downward attraction of the liquid over the upward attraction of its vapor, giving a resultant downward pull on the surface film, so that the space integral of this surface-force per gram may be taken as the specific inner heat of vaporization. A relation among heat of vaporization L_i, phase densities and temperature would follow therefrom. A kinetic theory calculation of it yields

$$dL_i = \frac{RT}{JM}\,\frac{vdv}{(v-b)^2}$$

or

$$L_i = \frac{RT}{JM}\left(\log\frac{v'-b}{v-b} + \frac{b}{v-b} - \frac{b}{v'-b}\right),$$

where R, T, M, b, v and v' denote gas-constant, absolute temperature, molecular weight, covolume and the specific volumes of liquid and of vapor. The same relation may be obtained easily, but less generally, from the Waalsian equation

$$p(v - b) = RT/M$$

by differentiating for constant temperature and combining with the equation $dp = \rho dV$ for hydrostatic equilibrium (ρ = density, V = potential of forces on the liquid) and integrating from the interior of the liquid to that of the vapor.

To test his equation the author employs it to calculate b at different temperatures for a dozen substances, and using this b thereupon to find the constant a of the van der Waals formula to test the constancy of this latter. He finds that b falls very slowly with rising temperature, but in such wise as to maintain a surprisingly constant. For propyl alcohol and carbon tetrachlorid the agreement is poor. Elimination of b from the two equations would not be the same thing, for a varies from the liquid to the vapor.

It is shown to follow that at low temperatures the total heat of vaporization is

$$JL = \frac{RT}{M} \log \frac{a}{pv'} + \frac{a}{v},$$

whence it is seen that Trouton's law will be much affected only by the variation, from substance to substance, of v', which only enters in the logarithm and in the denominator of a small term. *J. E. T.*

Note on the Vapor Pressure Curve. *M. Thiesen. Zeit. comp. flüss. Gase*, **1**, *13* (*1897*). The author recalls that when the Maxwell-Clausius equation

$$\int_{v_2}^{v_1} p dv = p_1(v_1 - v_2),$$

relating to the theoretical and actual vaporization isotherms, is transformed by supstituting $P_1 - P_2$ for its first member, one can evaluate $P_1 - P_2$ as $\int_2^1 s\,dt - \int_2^1 v dp$ along any desired path and thus utilize the equation without assuming a theoretical relation between p and v. He indicates several methods by which this might be done. *J. E. T.*

Note on the Heat of Vaporization. *M. Thiesen. Verh. phys. Ges. Berlin*, **16**, *80* (*1897*). Certain quantities, as $v_2 - v_1$, vanish at the critical point, while their differential coefficients become infinite; from which has been concluded that near the critical point these quantities are proportional to a fractional power of $\mathfrak{T} - T$,—where T denotes the absolute temperature and $\mathfrak{T}$ its value at the critical point. Thiesen has been led to assume this power to be *1/3*, which he finds to be in general correct. He finds also that the heat of vaporization ρ is closely proportional to $(\mathfrak{T} - T)^{1/3}$,

$$\rho = \mathfrak{r}(\mathfrak{T} - T)^{1/3}.$$

The best agreement is with water, where from 0° to 160° C the value of log $\mathfrak{r}$ only fluctuates by one unit of the fourth decimal place; at higher temperatures it slowly rises. Assuming the law of corresponding states, the quantity

$$\frac{\mu\rho_0}{\mathfrak{T}} = \mu\mathfrak{r}\mathfrak{T}^{-2/3}$$

should be constant for all bodies for which the relation holds (μ = molecular weight); it varies from 18 to 28 for eleven bodies. It is proposed to use the equation for approximative calculation of heats of vaporization. *J. E. T.*

On the Thermal Properties of Vapors; *Part VI. A. Battelli. Ann. Chim. Phys.* (*7*) **9**, *409* (*1896*). In continuation of his former researches the author, in the present paper, describes his measurements of the densities of CS_2, $(C_2H_5)_2O$ and C_2H_5OH at various temperatures and under the pressures of their saturated vapors. Two methods are employed. In the first a closed dilatometer is heated till the vapor space left in the drawn out point is negligible (as to mass of vapor), and the temperature noted, the volume coefficients of the glass for pressure and temperature having already been determined. In the second method the necessity of opening the dilatometer after each measurement is avoided by connecting it to a Cailletet pump which allows the liquid to be brought to the desired place in the fine point by merely working the pump. Curves and tables of results are given as well as the three sets of constants for an interpolation formula $S = a + b(t + 273) + c(t + 273)^2$. The results are not to be represented accurately by such a formula. A formula put in terms of the «corresponding» data represents the results fairly for points near the critical temperature. Formulas derived from those of Cailletet and Mathias and Clausius are incapable of representing the results of the author's experiments. *E. B.*

On the Pretended Existence of the Critical Density. *P. De Heen. Bull. Acad. roy. Belg. (3)* **33**, *119 (1897)*. The author, contending that the critical density of a fluid has never been directly observed, maintains that observation with his «analyzer of the critical state»,—Bull. Acad. roy. Belg. (3) **31**, 379 (1896),—shows the densities of liquid and of vapor to differ at the critical point. From Amagat's isotherm nets for carbon dioxid and for ether he claims to find the ratio of these densities to be 2.17 and 1.98 respectively, from which, admitting the theorem of corresponding states, he concludes that this ratio is sensibly equal to 2 for all bodies. Compare the following review. *J. E. T.*

The Vapor Pressures, Specific Volumes, and Critical Constants of Normal Pentane, with a Note on the Critical Point. *S. Young. Jour. Chem. Soc.* **71**, *446 (1897)*. Normal pentane boils at 36.3° under 760 mm pressure; the value of dp/dt at the boiling point is 25.8 mm per degree. The critical temperature is 197.2°, the critical pressure 25100 mm and the critical volume for one gram 4.303 cc. The author has determined the specific volumes of liquid and saturated vapor up to 197.1°. While it is practically certain that in all cases the densities of liquid and saturated vapor become equal at the critical point, it is very satisfactory to have one set of measurements demonstrating this point. *W. D. B.*

Relations between the Melting-points and the Latent Heats of Fusion of the Metals. *J. W. Richards. Jour. Franklin Inst.* **143**, *379 (1897)*. In 1893 the author asserted the heats of fusion of metals to be one-third their total heat capacity from −273° to the fusion temperature, and thus predicted the heat of fusion of gold to be 14 cal. It has since been found to be 16.3 cal. He now shows the rule to hold roughly for eleven metals and to fail for Al, Ga, Sn, Bi. The Al acts as diatomic in depressing freezing temperatures, and Sn and Bi disobey Pictet's rule, $ta\sqrt[3]{V} = 4.5$ (1), where t, a and V are the absolute melting temperature, the coefficient of expansion, and the ratio of atomic weight to atomic volume. Taking, from Dulong and Petit, $6.4 \times t$ as total heat capacity up to the melting temperature, and one-third of this as the atomic heat of fusion, he gets from (*1*) for the latter

$$L = 9.5/a \sqrt[3]{V}$$

which gives L with an average approximation of about 8 percent for eleven metals. Al remains an exception. The formula is then used to predict the heats of fusion of thirteen metals. *J. E. T.*

The Electrical Properties of Pure Sulphur. *R. Threlfall and J. H. D. Brearley. Phil. Trans.* **187** (A), *57* (*1896*). Sulfur was obtained by decomposition of sodium hyposulfite or of calcium polysulfids with hydrochloric acid, as well as by the Chance process. It was purified by repeated distillation, never by crystallization. The melting point of rhombic sulfur is 116°, of monoclinic sulfur 120°. The specific resistance of pure monoclinic sulfur is above 10^{28} c.g.s. units, but the admixture of five percent of amorphous sulfur reduces this to 10^{25} c.g.s. units. The conductivity is always greater for three or four minutes after the battery is reversed. The conductivity increases enormously with rising temperature.

W. D. B.

On the Enantiomorphism of the Benzene Derivatives. *W. Vaubel. Jour. prakt. Chem.* (*2*) **55**, *221* (*1897*). The author gives reasons to show that his formula for benzene is not necessarily wrong because there are no isomeric disubstitution products. *W. D. B.*

Studies on the Formation and Inversion of Solids. First Paper: Supersaturation and Supercooling. *W. Ostwald. Zeit. phys. Chem.* **22**, *289* (*1897*). An experimental paper by Ostwald is always a treat and this one is no exception to the rule, illustrating, as it does, the remarkable ingenuity and manipulative skill of the author. It was found that, at ordinary temperatures, salol (melting-point 39.5°) will remain indefinitely in the liquid state if kept out of contact with the solid phase. The author then set himself the apparently hopeless task of determining what quantities of solid salol could be added without causing the liquid to crystallize. To dilute the solid salol, it was rubbed together with milk sugar or quartz powder, a small portion of this was ground up with more of the indifferent solid and this operation repeated as often as proved necessary. In the actual experiments the concentration of the salol in the mixture was reduced to one-tenth its value by each successive dilution so that in one gram of the mixture D_3, for instance, there would be one milligram of solid salol. It was found that D_3 caused the supercooled liquid to crystallize while D_4 did not. Since about 0.1 mg was taken for the test we have the result that 10^{-8} g salol will not cause crystallization while 10^{-7} g will. This however is not a fair way of stating the case since a much smaller quantity of pure salol would cause precipitation. This is shown by the fact that a mixture D_6 will cause crystallization when freshly prepared; but loses this power on standing, even in closed vessels. The explanation of this phenomenon is that with increasing relative surface of the indifferent substance we get adsorption of the salol probably as gas and it is therefore no longer present as a solid. If an appreciable time is necessary to reach equilibrium, that would account for the dilutions $D_4 - D_6$ becoming inactive on standing. An interesting conclusion that one may draw from this but which was not tested by the author is that the dilution at which the salol no longer acts as a solid must vary with the fineness of the indifferent powder.

With sodium thiosulfate D_6 is the first dilution which is inactive. When first made up, D_5 is still active and the author attributes the change with the time to a decomposition of the salt though there is no reason given for not applying the same explanation as with salol.

The author next takes up the question whether below a given temperature there may be formation of the solid phase in the case of supercooled liquids. This was the more probable since experiments by Moore in the Leipzig laboratory had shown that liquid phenol can not be cooled below 24°. With parachlornitrobenzene the author finds that spontaneous formation of the solid phase never takes place above 77° but may below it. Since the melting point of this substance is 83°, the system, liquid and vapor, is in metastable equilibrium between 83° and 77° and in labile equilibrium below this latter temperature. The reviewer has not shared Ostwald's objection to the word «labile» in the past; but he is glad to acknowledge that these experiments justify a distinction between «labile» and «metastable» states.

A consequence of this distinction is that it is theoretically possible that a system which is in instable equilibrium with respect to two solid phases may be in labile equilibrium with respect to the one phase and in metastable equilibrium with respect to the other. In the case of a supercooled liquid ***at temperatures below the triple point for two solid phases and vapor*** the equilibrium is more likely to be labile with respect to the less stable than with respect to the more stable modification and one might reasonably expect the former to appear spontaneously. This is often the case and Ostwald puts forward the general law: «On passing from any state to a more stable one, there will be formation of the nearest and not of the most stable modification.» Four pages are devoted to a consideration of this hypothesis; but no attempt is made to show any relation between it and the «labile» and «metastable» equilibria except in the one case cited. It might have been mentioned that this same hypothesis had already been put forward tentatively, this Journal **1**, 142 (1896).

After a brief discussion of the difference between monotropic and enantiotropic substances, the author passes to a consideration of the amounts of salt necessary to produce crystallization in supersaturated solutions and shows how this might be used to detect the presence of very small quantities of certain salts. One curious slip is made here. It was noticed that effloresced crystals of hydrated sodium sulfate worked as satisfactorily as crystals fresh from the solution and the conclusion is drawn that efflorescence has no effect. Since the crystals became inactive after heating above 33° the obvious conclusion is that the crystals had not completely effloresced. Whether this was due to insufficient exposure to the air or was an inherent property of hydrated salts could then be determined.

Although there are some minor defects in the treatment, the paper is a classic and will be a source of inspiration to many for years to come. *W. D. B.*

Contributions to the Determination of Molecular Weights. V. *E. Beckmann. Zeit. phys. Chem.* **22**, *609 (1897)*. Acetic acid, benzoic acid and *α*-benzaldoxim do not form solid solutions with benzene. Thiophene does and the ratio of the concentrations in the two phases is fairly constant. At temperatures above 800° selenium has a lower vapor pressure than corresponds to the formula Se_2; but this increases with rising temperature. In phosphorus as solvent, selenium seems to be represented by the formula Se_8. The author describes a method of stirring a solution without admitting moisture, using a mercury joint. *W. D. B.*

Cryoscopic Experiments to determine the Constitution of Tropanin and Granatanin. *F. Garelli. Gazz. chim. Ital.* **27**, *I, 384 (1897)*. Both substances behave normally in benzene, abnormally in naphthalene, confirming the formulas of Merling and of Ciamician. *W. D. B.*

Reply to Some Comments of Herr Bodländer. *F. Garelli. Gazz. chim. Ital.* **27**, *I, 247 (1897)*. The author states that his main object in experimenting with phenol and benzene was to show that solid solutions were formed and not to study the distribution ratio; that his results were calculated correctly, he having referred the concentrations to one hundred grams of solvent instead of to one hundred grams of solution; and, lastly, that he thinks Bodländer's hypothesis of single molecules in solid benzene and double ones in liquid benzene no better established than his own that the distribution coefficient varies very much with the temperature. *W. D. B.*

Cryoscopy of Precision. *F. M. Raoult. Bull. Soc. Chim. Paris, (3)* **15**, *1153 (1896)*. **Reply.** *A. Ponsot. Bull. Soc. Chim. Paris, (3)* **17**, *162 (1897)*. Raoult begins «I desire to present here in some detail the results of very careful experiments which I have made on the freezing points of aqueous solutions of sodium chlorid: the surroundings being either at the temperatures of the freezing points or a few degrees lower. This will be, I hope, the best way to answer M. Ponsot's criticism of my last article», this Journal **1**, 252.

The author defines the ‹temperature of convergence› to be that attained by a liquid in his apparatus when the stirrer is kept at a certain constant velocity and the freezing bath at a fixed temperature; it is generally 0.25°C above the temperature of the freezing bath. As a result of the experiments it appears that the *apparent* depressions (when the temperature of the bath is 3.5°C below the temperature of convergence) are 0.2 percent greater than the *true* depressions (*i. e.* those observed when the temperature of the bath and that of convergence are the same). The experimental error is set at about 0.001°C. The value of the depression for infinite dilution (extrapolation) agrees well with that calculated on the hypothesis of total ionization. Ponsot's results are explained by the insufficient vertical agitation of the solutions in his apparatus.

In his reply Ponsot argues that four out of the five points in the criticism referred to are either passed over or conceded by Raoult, and that the latter's new experiments prove nothing, as in four cases out of six the difference between ‹apparent› and ‹true› freezing points lies within the errors of observation. *W. L. M.*

Details of the Method followed in Accurate Cryoscopic Measurements. *F. M. Raoult. Comptes rendus*, **124**, *851* (*1897*). The author describes two experimental methods for determining the excess of the convergent temperature over that of the bath. He recommends keeping the thermometer on ice when not in use, in order to prevent changes in the zero reading. *W. D. B.*

Influence of the Superfusion on the Freezing-points of Solutions of Sodium Chlorid and of Alcohol. *F. M. Raoult. Comptes rendus*, **124**, *885* (*1897*). The author plots the degree of supercooling against the observed lowering of the freezing point and finds, by extrapolation, the lowering for no supercooling. These results show that the error introduced by a constant amount of supercooling is not independent of the concentration, as the author had hitherto assumed. *W. D. B.*

The Melting Points of Some Organic Compounds. *B. v. Schneider. Zeit. phys. Chem.* **22**, *225* (*1897*). The author finds, in agreement with Landolt, that accurate melting point determinations can be made only when the thermometer is surrounded by large quantities (20 grams or more) of the substance in tubes of 2–3 cm diameter, provided with a stirrer. If capillary tubes be employed, as in the ordinary laboratory methods, the temperatures observed are oftenest too high, sometimes however too low. In determining the temperatures (mostly below zero, and some as low as – 142°C) the thermometer was in many instances replaced by a thermoelectric couple constantan-iron. Liquid air was employed as a freezing bath. *W. L. M.*

Determination of the Constitution of the Amids by means of Cryoscopic Measurements. *A. Lachman. Zeit. phys. Chem.* **22**, *170* (*1897*). An attempt to decide between the two tautomeric formulas for oxamethane ($NH_2.CO.CO_2C_2H_5$, and $NH:COH.CO_2C_2H_5$) by determination of molecular weight (freezing point) in methyl oxalate. Molecular weights as high as 226 (calc. 117) were found in concentrated (13 percent) solutions; the author considers this as evidence of the presence of an hydroxyl group—second formula above—while the indifference of the oxamethane towards phosphorus trichlorid is an argument in favor of the first formula.

The cryoscopic constant of methyl oxalate as determined by the freezing points of solutions of naphthalene, is 53.5. *W. L. M.*

The Lowering of the Freezing-point of Magnesium Chlorid by Addition of Other Substances. *J. H. van 't Hoff and H. M. Dawson. Zeit. phys. Chem.* **22**, *598* (*1897*). By freezing-point of magnesium chlorid is meant inversion temperature for $MgCl_2 6H_2O$ and $MgCl_2 4H_2O$. The molecular lowering is 76. Potassium and sodium chlorids give this value while potassium sulfate gave at first three times it; but the freezing point rises as a double salt separates.

W. D. B.

Combinations of Ammonia Gas and of Methylamin with the Haloid Salts of Lithium. *J. Bonnefoi. Comptes rendus*, **124**, *771* (*1897*). A preliminary note on the dissociation pressures and heats of formation of the addition compounds with lithium chlorid.

W. D. B.

Dissociation Pressure of Alkylammonium Hydrosulphides. *J. Walker and J. S. Lumsden. Jour. Chem. Soc.* **71**, *428* (*1897*). The authors have determined the vapor pressures, at different temperatures, of ammonium, dimethyl ammonium and ethyl ammonium hydrosulfids. They then studied the dissociation pressures of binary mixtures of these substances. In all three cases the pressure is lower than the value calculated from the mass law equations. When ammonium hydrosulfid is one of the components, the vapor pressure of the mixture is less than that of pure ammonium hydrosulfid. The authors were unable to find a satisfactory explanation for this very interesting phenomenon.

All attempts to determine the dissociation pressure of methyl ammonium hydrosulfid failed, possibly owing to the formation of another solid phase at 39°. From the pressure-temperature curves for the other hydrosulfids the authors were able to deduce the conclusion that the heat of reaction increases with rising temperature.

W. D. B.

The Freezing-points of Alloys containing Zinc and Another Metal. *C. T. Heycock and F. H. Neville. Jour. Chem. Soc.* **71,** *383 (1897).* No compounds crystallize from solutions containing zinc and cadmium, aluminum or tin. With zinc and tin there is a curious change of curvature in the curve along which zinc is solid phase, and a similar, though much less marked, change occurs with the system, zinc and aluminum, in the curve along which aluminum is solid phase. Zinc is only partially miscible at its melting point with bismuth, thallium, lead, antimony, magnesium and nickel. The complete freezing-point curve was determined only for zinc and bismuth. Addition of gold, copper or silver to zinc raises the freezing-point of zinc while addition of platinum up to four percent seems to have no effect. Of these last four systems only the one for silver and zinc was studied in detail. The curve consists of five distinct parts and the phenomena can best be explained on the assumption that the order of crystallization is: solid solution of silver in zinc, $AgZn_2$, AgZn, Ag_2Zn, Ag, no one of the three compounds being stable at its melting point.

From the measurements in dilute solutions with the metals which lower the freezing-point of zinc, excluding the results with aluminum, the authors calculate 28.33 cal for the heat of fusion of one gram of zinc, while Person found 28.13 experimentally. The reviewer wishes to call attention, without comment, to the following quotation: « In order that our work might have the value attaching to an independent investigation, we have not allowed ourselves the pleasure of studying his [Gautier's] paper, although very possibly we might have been saved from some errors by doing so ». *W. D. B.*

Divariant Systems

On the Calculation of C_p/C_v by the Method of Clement and Desormes. *R. Swyngedauw. Jour. de Phys. (3)* **6**, *129* (*1897*). In the usual method of making this calculation the change of volume due to the rise of the liquid in the manometer is neglected. This introduces an error which is not always inappreciable. The author shows how the proper correction may be calculated. He concludes that since the law of Boyle does not come in, except in the calculation of this correction, the method is capable of giving exact results for all gases. It is not necessary to know their laws of isothermal compression if only the final pressure in the adiabatic change is read accurately. *E. B.*

A Contribution to our Knowledge of the Equation of Condition. *J. D. van der Waals. Kon. Akad. Wetensch. Verslag, Amsterdam*, **1896-97**, *150* (*1897*). An investigation in the kinetic theory of gases, to find how the covolume b of van der Waals's equation depends upon the volume V. As first approximation is found

$$b = b_\infty(1 - 17b_\infty/32V)$$

b_∞ denoting the value of b in indefinitely great volume. The way of calculating further correction terms is indicated. *J. E. T.*

Remarks Concerning the Law of Corresponding States. *J. D. van der Waals, Jr. Kon. Akad. Wetensch. Verslag, Amsterdam*, **1896-97**, *248* (*1897*). The densities of ether, carbon bisulfid and alcohol as determined by Battelli and those of alcohol as found by Young are compared with the law of corresponding states, and certain statements of Young and of Gräz regarding the law are corrected. *J. E. T.*

On the Entropy of a Mass of Gas. *H. A. Lorentz. Kon. Akad. Wetensch. Verslag, Amsterdam*, **1896-97**, *252* (*1897*). A kinetic gas theory calculation to show that under the usual assumptions the entropy of a gas is $-\frac{2}{3}\mu H$, where H is Boltzmann's minimum function and μ is k/θ, k being the average kinetic energy of a «molecule» and θ the absolute temperature. *J. E. T.*

On the Critical Conditions, the Conditions of Folding, of a Mixture. *J. D. van der Waals. Arch neérl.* **30**, *278* (*1896*). The differential equation of the line of folding, deduced in an earlier paper —see this Journal **1**, 313—is found by differentiating the function

$$p[\tau, x(\tau), V(\tau)],$$

where p, τ, x and V are the pressure, absolute temperature, composition and volume at the critical point, and then introducing the condition characteristic of the line of folding. From one of the intermediate equations the author concludes that the stability of a critical phase is the greater the higher the temperature. He recalls that, the composition of a binary mixture being given, the remaining conditions of the critical state are determinate; p, V and τ are functions of x, and the differential equations involving them are likewise determinate. He indicates the route to be followed in seeking these latter relations, and introduces a series of comments on the special points which arise by the way. *J. E. T.*

On the Molecular Pressure, II. *G. Bakker. Zeit. phys. Chem.* **22**, *277* (*1897*). Writing

$$d\varepsilon = dh + dV,$$

(Zeit. phys. Chem. **12**, 672) for the differential of the energy of a homogeneous body, where h is the «absolute heat capacity» and V the «potential energy», combining this equation with the assumption that V is the potential energy of the attractive forces of the molecules, and integrating, the author finds for the «molecular pressure» (which together with the «thermal pressure» makes up the total pressure)

$$K = T\varphi(v^2 T).$$

If this molecular pressure is to be represented by a volume function the only solution is

$$K = Ta/v^2 T = a/v^2$$

the van der Waals form. *J. E. T.*

On the Application of the Kinetic Theory to Dense Gases. *S. H. Burbury. Phil. Trans.* **187** (A), *1* (*1896*). In all systems of a great number of elastic spheres, whose aggregate volume is not negligible against the containing space, there exists a tendency for the spheres to move together in streams, and so to diminish the mean pressure. Boltzmann's minimum function when minimum differs by a quantity $\frac{1}{2}\log D$ from the value which it would have for material points. *J. E. T.*

Observations on the Properties of Some Highly Purified Substances. *W. A. Shenstone. Jour. Chem. Soc.* **71**, *471* (*1897*). Working with the electrical discharge and moist oxygen at 0°, 13.5 percent of oxygen was converted into ozone. With moderately dried oxygen (pressure of water vapor estimated at 0.0001 mm) only 11.1 percent of oxygen could be changed. Ozone is fairly stable in moist oxygen, very instable in dried oxygen. The rate of change is roughly thirty times as high in dried oxygen at zero as in moist oxygen at 26.4°. With very dry oxygen only 0.2 percent was changed into ozone.

The action of chlorin, bromin and iodin on mercury is independent of the presence of water vapor. The abnormal expansion of chlorin in sunlight, noted by Budde and by Richardson, does not occur with highly purified chlorin. *W. D. B.*

Some Experiments upon the Evaporation of Liquids by a High Gas Pressure. *N. Schiller. Wied. Ann.* **60**, *755* (*1897*). At 25° nearly three times as much ether will dissolve in a given volume containing air under 115 atm pressure as in the same volume filled with air under atmospheric pressure. With chloroform the corresponding ratio is nearly two and one-half. The author prefers to look upon this as a case of squeezing vapor out of the liquid rather than to speak of increased volatility. *W. D. B.*

Some Experiments on Helium. *M. W. Travers. Proc. Roy. Soc.* **60**, *449* (*1897*). If a vacuum tube provided with platinum electrodes be filled with helium and the discharge passed, the gas is absorbed by the platinum (splashed off) on the walls of the tube ; and the color of the glow changes gradually from yellow to green. On heating the tube the absorbed gas is liberated again and the yellow color is restored. In order to ascertain whether the helium employed consisted of a mixture of a ‹yellow› with a ‹green› constituent the discharge was interrupted when the green had reached its maximum intensity, the gas remaining in the tube removed by pumping and then the absorbed fraction liberated by warming. «Now if any separation had taken place the gas which had been absorbed by the platinum should contain a larger proportion of the yellow constituent of helium and should give a yellow glow in a vacuum tube even at low pressure. The current was turned on and a glow appeared of the green color invariably shown by helium at low pressures. The change of color in the tube during absorption of the helium is to be entirely attributed to the lowering of the pressure».

Advantage may be taken of this property of helium to separate it from argon. *W. L. M.*

Communication regarding Investigations with the Micromanometer. *A. Smits. Kon. Akad. Wetensch. Verslag, Amsterdam,* **1896-97,** *292 (1897).* The author's micromanometer (l.c., 1895), giving measurements accurate to 0.0033 mm water or 0.00024 mm mercury was used to determine the vapor pressures at 0°C of aqueous solutions with concentrations varying from 0.01 to 2.64 molecular weights per 1000 grams of water. With sodium chlorid and potassium hydroxid the vapor pressure fell more rapidly than the concentration, van 't Hoff's coefficient *i* rising considerably with rising concentration,—a result incompatible with the electrolytic dissociation theory. For cane sugar *i* is very near unity, save for the highest concentration where it becomes 1.115. Calculating *i* for the two electrolytes, upon the assumption that $NaCl.2H_2O$ and $KOH.5H_2O$ are the dissolved bodies, it is found to remain very constant at 1.65. It was observed accidentally that anilin vapor is absorbed appreciably by concentrated sulfuric acid only in the presence of water vapor.

J. E. T.

On the Question whether the Maximum Tension of a Vapor depends upon the Temperature alone. *V. A. Julius. Kon. Akad. Wetensch. Verslag, Amsterdam,* **1896-97,** *295 (1897).* From careful measurements with Smits's micromanometer it is concluded that the pressure of vapor in equilibrium with pure liquid depends only upon the temperature, but that the presence of a gaseous impurity may give rise to variation with certain limits, the final pressure depending upon the manner in which the final state is reached. Critical reference is made to similar measurements by Tammann and by Wüllner and Grotrian. *J. E. T.*

Equilibrium in Systems of Three Components whereby Two Liquid Phases can appear. *F. A. H. Schreinemakers. Zeit. phys. Chem.* **22**, *93* (*1897*). The present paper is the first of a series in which Schreinemakers promises to discuss the equilibria of ternary systems with the aid of the Gibbsian thermodynamic potential surface. This programme is an interesting one, for very extensive classes of equilibria are possible in such systems and they have not as yet been made the subject of much study. The present paper gives a purely theoretical treatment of the successive possible states of equilibrium in systems where two liquid phases can appear, with or without a solid phase. This is done under the assumption that no pair of the components can alone form two liquid layers, a state of affairs of which probably no actual example is known.

The composition, of the liquid mixture, is represented by the points in an equilateral plane triangle, and the corresponding thermodynamic potentials for constant temperature and pressure appear as ordinates drawn from these points—thus producing a ‹potential surface›. Corresponding to the appearance of two liquid phases a ‹fold› is introduced into the surface, over which a bitangent plane rolling from a plaitpoint (point of folding) and therefore touching at conjugate points marks out binodal curves whose horizontal projections, together with that of the included spinodal curve, are assumed to be closed curves with but two plaitpoints. Any point within the binodal curve represents an instable solution, which must separate into two liquid phases having the composition represented by the conjugate points ; for the potential of the system is the less in the latter state. A proof is then offered for the statement that the horizontally projected locus of the points of contact of bitangent straight lines in vertical planes passing through an apex of the triangle lies within the projection of the binodal curve, although the spinodal curve may cut this locus.

Under the appearance of a solid phase is treated only the simplest case, where this phase is composed of one of the solid components. The thermodynamic potential of the solid being represented by a point on the ordinate of the corresponding apex of the triangle, the composition of the liquid phases which can be in equilibrium with it are represented by the horizontal projection of the curve of contact of the potential surface with a cone which touches the surface and has its apex at the point. The different possible stable and instable states of the system are then deduced from the geometrical properties of the surface, and a detailed discussion of the stable states is given. The whole treatment is simplified by the assumption that the binodal curve lies entirely within the triangle, that but one solid phase can appear, that but a single fold occurs in the surface, etc. So the paper, interesting as it is, is far from being the general theoretical treatment of the equilibria of ternary systems which must eventually follow this initial effort. *J. E. T.*

Methods of Determining the Molecular Weights of Homogeneous Liquids. *J. Traube. Ber. chem. Ges. Berlin*, **30**, *265* (*1897*). As the result of a detailed review of the various methods proposed for ‹ascertaining the molecular weights› of liquids and solids, the author concludes that there is essential agreement between the figures obtained more or less directly, from measurements of optical refraction, surface tension, viscosity, compressibility, the critical constants and the latent heat of evaporation. In the large majority of cases the molecular weights so defined agree with those obtained from determinations of the vapor density. *W. L. M.*

The Law of the Contraction observed on dissolving Sugar in Water. *A. Wohl. Ber. chem. Ges. Berlin* **30**, *455* (*1897*). The ‹density of a 100 percent sugar solution› (obtained by extrapolation from Scheibler's empirical formula) is made the basis of a series of calculations, under the title of ‹The Specific Gravity of Liquid Sugar›; the contraction is the difference between the volume of a given sugar solution and the volumes of the water and ‹liquid› sugar it contains. By setting the contraction per unit volume proportional to the quantities of sugar and of water respectively contained in the unit volume of the solution, the author obtains an equation involving two constants, which gives the volumes of aqueous sugar solutions accurately to four decimal places. *W. L. M.*

Influence of Pressure on Change of State. *A. Ponsot. Comptes rendus,* **123**, *595, 648 (1896).* The experiments of Villard have shown that if a system consisting of a liquid *A* and a gas *B* be subjected to pressure, the partial pressure of the vapor given off by the liquid is increased ; he ascribes this result to a «dissolving action» of the gas. In his first paper the author shows that, in the limiting case, when the gas *B* is insoluble in *A*, the influence of pressure on the vapor tension of the latter may be expressed by a thermodynamical formula deduced by means of a cyclical process involving the introduction of osmotic pressure, etc. In the second he takes up the case where *B* is soluble ; and shows that the partial pressure of *A* will be decreased by compression if the specific volume of *B* be greater in the gaseous phase than in the liquid, and vice versa, and that the degree of variation depends in a calculable manner upon the relation between the specific volumes of *B* in the two phases.
W. L. M.

On the Influence of Water on the Solubility in Alcohol and Ether of Some Substances containing Water of Crystallization. *E. Bödtker. Zeit. phys. Chem.* **22**, *505 (1897).* The solubility of cupric chlorid and of cobaltous chlorid in alcohol decreases slightly on addition of water. This is attributed to a change in the medium. From the increase in concentration on adding more water the author concludes that we have in solution, $CuCl_2H_2O$, H_2O and $(H_2O)_2$ in the one case and $CoCl_25H_2O$, H_2O and $(H_2O)_2$ in the other. Unfortunately the author does not discuss the changes that would take place in the dissolved $CoCl_25H_2O$ on further addition of water. Since more water dissolves in ether containing oxalic acid than in pure ether, the author claims to have proved the existence of a hydrate in the ethereal solutions. Since it is a perfectly general phenomenon that addition to two partially miscible liquids of a substance soluble in both increases the miscibility of the two liquids, the author's conclusion is unjustifiable. *W. D. B.*

On the Distribution Coefficient and Abnormal Diffusion. *G. Tammann. Zeit. phys. Chem.* **22**, *481 (1897).* The author calls attention to the fact that the distribution coefficient must be unity when two phases become identical. Several instances are given of apparently abnormal diffusion with dyestuffs; but the author fails to appreciate the important part due to the relative solubilities.

W. D. B.

A New Series of Mixed Sulphates of the Vitriol Group. *A. Scott. Jour. Chem. Soc.* **71**, *564* (*1897*). By adding sulfuric acid to a solution containing two vitriols, crystals are obtained containing less than the normal amount of water. The results which the author publishes are practically valueless because he does not recognize that he is investigating a series of solid solutions. To take a single example, it is very improbable that any such compound as $CuFe_2(SO_4)_2 3H_2O$ exists. *W. D. B.*

Action of High Temperatures on the Peroxid of Antimony. *H. Baubigny. Comptes rendus,* **124**, *560* (*1897*). Antimonic acid changes into antimony peroxid at temperatures below the melting point of silver. At higher temperatures, but below the melting point of gold, the peroxid decomposes into oxygen and volatile antimonious acid.

W. D. B.

On the Electrical Absorption of Nitrogen by Carbon Compounds. *M. Berthelot. Comptes rendus,* **124**, *528*; *Ann. Chim. Phys.* (*7*) **11**, *35* (*1897*). Under the influence of the electric discharge nitrogen forms compounds with benzene, thiophene, carbon bisulfid and other substances. *W. D. B.*

Effect of the Corresponding Acids or Bases upon the Solutions of Haloid Salts. *A. Ditte. Ann. Chim. Phys.* (*7*) **10**, *556* (*1897*). A complete account of experiments upon the precipitation of salts, some of which have already been noticed in this Journal **1**, 382 (1897). Sodium iodid shows a continuously decreasing solubility in presence of hydriodic acid and a discontinuously decreasing solubility in presence of sodium hydroxid. The curve for this latter solution is very remarkable. It is composed of three distinct parts, the concentration of sodium iodid remaining absolutely constant along the middle portion. Since the salt with two of water is supposed to effloresce directly to the anhydrous salt, this type of curve is anomalous.

W. D. B.

On the False Equilibria with Selenium Hydrid. *H. Pélabon. Comptes rendus*, **124**, *360* (*1897*). Above 325° the same equilibrium is reached whether selenium hydrid be allowed to dissociate or hydrogen and selenium to combine. Below 325° this is no longer true and the author has determined the field within which a false equilibrium is possible. The results confirm the theory of Duhem.

W. D. B.

Concerning the Action of Hydrochlorid Acid on Metallic Sodium at Low Temperatures. *E. Dorn and B. Völlmer. Wied. Ann.* **60**, *468* (*1897*). The purpose of the paper is to explain the apparent inactivity of sodium on hydrochloric acid at −80°C. For this purpose various constants were measured.

The molecular conductivity of a solution of hydrochloric acid in water, of sp gr 1.1211 at 18°/4° = 24.3 percent HCl, was measured and found to follow the equation $\lambda = 10^{-8}(5065.0 + 95.753t + 0.2706t^2 - 0.002084t^3)$ down to $t = -82.2$ fairly well, the maximum deviation being an excess of calculated over observed value of 1.60 percent.

The coefficient of viscosity of the same solution was found to be 0.01635 at 15.64° and 0.9000 at −79.3°. For a solution of 1.56 percent lithium chlorid in methyl alcohol, the coefficient of viscosity was found to be 0.00797 at 15.56° and 0.0707 at −79.3°.

The density of the same solution at −78.4° was 1.174.

The potential of Na|HCl|Pt at −80° = 3.018V; p.d. of Zn|HCl|Pt at 13° = 1.450V. When Zn only cooled to −80°, p.d. = 1.172V; Pt only cooled to −80°, p.d. = 1.479V; Zn and Pt cooled to −80°, p.d. = 1.187V. The same solution, 24.3 percent HCl, was probably used.

After contact of sodium with hydrochloric acid solution for 12 minutes at −80°, 0.991 grams of the liquid contained 7.4 mg NaCl, while 10.4 grams of acid not in contact with Na left a residue of only 0.5 mg.

C. L. S.

Polyvariant Systems

On the Decomposition and Formation of Hydriodic Acid. *M. Bodenstein. Zeit. phys. Chem.* **22**, *1* (*1897*). The author's previous experiments, Zeit. phys. Chem. **13**, 56 (1894), on velocity and equilibrium at various pressures and temperatures gave results which did not agree with the predictions of the mass law. In the present investigation a measurement of *all* the quantities of hydrogen, iodin and hydriodic acid, both before and after the reaction, led to the discovery that the glass bulbs act on the hydriodic acid, partly by the formation of sodium iodid and partly by some sort of absorption. This action is different for different kinds of glass, is proportional to the surface, is dependent on the temperature and is independent of the amount of hydriodic acid present. When corrected for this error the results of this paper and the earlier one are in satisfactory agreement with the scheme $H_2 + I_2 \rightleftarrows 2HI$. *E. B.*

Researches on the Compressibility of Solutions. *H. Gilbault. Ann. Fac. Sci. Toulouse* **11**, *B 1 (1897)*. As the result of a great many very interesting measurements on the compressibility of solutions the author reaches the following conclusions. «The difference between the critical temperature of a solution and that of the solvent depends only upon the number of molecules of the solid solute and not upon its chemical nature. A liquid and the solutions made with this liquid conform to the theorem of corresponding states ; the true compressibilities at the temperature t and the pressure p are given by the equation :

$$y = \frac{a - b.p/\pi}{\frac{\theta - t}{273 + t} + d\frac{p - \pi}{\pi}}$$

Water and aqueous solutions present anomalies at ordinary temperatures.

For a given temperature the compressibilities of solutions are given by the equation :

$$\frac{\log \mu_0 - \log \mu}{a} \cdot \frac{d'}{d} = k,$$

where μ_0 and d are the compressibility and density of the solvent, μ' and d' the corresponding terms for the solution, a the molecular concentration and k a constant.

The author calculates the molecular concentrations in a peculiar way, taking one-half the normal molecular weight of all solutes as representing the true reacting weight. While this may be permissible for potassium or sodium chlorid in water, it needs justification when applied to sodium carbonate in water and to benzoic acid or borneol in ether. *W. D. B.*

On the Chemical Theory of Solutions. *A. A. Jakowkin. Jour. Russ. Soc.* **29,** *I, 3 (1897).* In studying the nonelectrolytic dissociation $KI_3 = KI + I_2$ the author deduced the amount of dissociation from the distribution coefficient. He looks upon the solvent CS_2 or CCl_4 as a thin layer, permeable only to iodin, between the potassium iodid solution and pure water. If this layer is in equilibrium with both solutions or if both distribution coefficients for the different concentrations of iodin are known, the (active) mass of the iodin set free may be found from the amount of iodin in the corresponding aqueous solution. It thus becomes possible to write the equation for the dissociation isotherm. For the general case of a dissociation of the form, $AH_2O = A + H_2O$, there is found (see this Journal **1,** 65) an equation

$$\frac{p - p'}{p} = \frac{n}{N(1 + kv)}$$

which differs from that of Raoult only by a very small correction term, as is also the case with the author's formula for the osmotic pressure, $PV(1 + kv) = RT$.

The term kv expresses the variations which occur in concentrated solutions and, according to the author, this value increases in the special case owing to the formation of KI_3, in general however owing to the combination of the solute with the solvent. *E. St.*

The Relative Weights of Gold and Silver dissolved by Potassium Cyanid Solutions from Alloys of these Metals. *J. S. Maclaurin. Jour. Chem. Soc.* **69,** *1276 (1896).* A solution of potassium cyanid dissolves gold and silver from an alloy of these two metals in the same proportion in which they exist in the alloy. When the metals are separate, the quantities dissolved from equal surfaces are as their atomic weights. In the alloy, let A = weight of gold, B = weight of silver, then the relative areas of the metals exposed to cyanid solution are A/19.3 and B/10.45, the denominators being the specific gravities of the metals. Should the same relation hold for the alloy as for the separate metals—

Weight of gold dissolved = (A/19.3)196.8 = A 10.2.

Weight of silver dissolved = (B/10.45)107.66 = B 10.3, which agrees with the experiment. *C. L. S.*

An Experiment with Gold. *M. Carey Lea. Am. Jour. Sci.* (*4*) **3**, *64*; *Zeit. anorg. Chem.* **13**, *447* (*1897*). On mixing solutions of gold chlorid and sodium hypophosphite, a transparent green liquid is obtained which gradually becomes cloudy. The green is due to the formation of small quantities of the blue modification of gold in the naturally yellow solution. *W. D. B.*

Researches on the Reactions Between Gases. *H. Hélier. Ann. Chim. Phys.* (*7*) **10**, *521* (*1897*). Hydrogen and oxygen combine to a measurable extent at 180° and to a greater extent as the temperature rises. This is not a reversible reaction, for water vapor does not dissociate perceptibly even at 500°. The author has studied one of the limiting curves for false equilibrium and his experimental work is therefore of great importance. Some measurements made in tubes other than platinum showed that alkali is dissolved from glass and that the silver in silvered glass tubes is first oxidized and then dissolves in the glass. When glass tubes are used the reaction runs to an end and it was this one fact which kept van 't Hoff and V. Meyer from discovering the real nature of the phenomena. Measurements with mixtures of carbon monoxid and oxygen showed that an equilibrium is soon reached bearing no relation to the equilibrium due to the dissociation of carbon dioxid. *W. D. B.*

Theory of Reaction in Gases. *H. Hélier. Ann. Chim. Phys.* (*7*) **11**, *78* (*1897*). An attempt to apply the principles of thermodynamics to reactions in gases in such a way as to account for the phenomena observed experimentally. The attempt fails because the author has confused one of the limiting curves for false equilibrium with the theoretical equilibrium curve. *W. D. B.*

On the Expansion in Solutions of Ammoniacal Salts and of Sodium Hyposulfite. *U. Schiff and U. Monsacchi. Gazz. Chim. Ital.* **27**, *I*, *117* (*1897*). There is an increase in volume when ammonium nitrate dissolves in water, the percentage expansion rising as the solution becomes more saturated. If the water contains HNO_3, KNO_3 or NH_4Cl the expansion is much greater. Ammonium nitrate dissolves in methyl alcohol with contraction. Ammonium chlorid and bromid dissolve in water with contraction, ammonium iodid with expansion. Hydrazin hydrochlorid dissolves with contraction while hydroxylamin hydrochlorid and sodium hyposulfite go into solution first with decrease, then with increase of volume. *W. D. B.*

On the Conditions for the Direct Combination of Sulfur and Hydrogen. *H. Pélabon. Comptes rendus,* **124,** *686 (1897).* Above 440° the same equilibrium is reached whether one starts from hydrogen sulfid or hydrogen and sulfur. Below this temperature this is not the case although hydrogen combines with sulfur even at 215°. The author has determined the amount of hydrogen sulfid formed at temperatures ranging from 220° to 350°, the other conditions being the same. He is dealing with a case of false equilibrium. *W. D. B.*

On the Equilibrium between Amalgams and Electrolytes. *A. Ogg. Zeit. phys. Chem.* **22,** *536 (1897).* The reaction between mercury and silver nitrate does not run to an end and may be expressed by the equation: $Hg + AgNO_3 \rightleftarrows Ag + HgNO_3$. Since the silver combines with the mercury to form an amalgam its active mass is variable and the relative concentrations of the nitrates may vary. The author has applied the mass law formula to this equilibrium, keeping the total amount of mercury constant. His experiments confirm the formula fairly well. It is conceivable that he might have got a yet better result if he had not ignored the changes in the concentration of the mercury. *W. D. B.*

Oxidation of Nitrogen by the Electric Spark and Arc. *F. v. Lepel. Ber. chem. Ges. Berlin,* **30,** *1027 (1897).* The current from a Ruhmkorff coil is passed between electrodes of various materials in an atmosphere filled with spray from an atomizer. The yield of the oxids of nitrogen depends largely on the form of the glass vessel containing the electrodes; it is improved by increasing the current, by lengthening the path of the sparks and by passing a current of air through the apparatus and thus removing the products of oxidation from the neighborhood of the electrodes. If oxygen be added to the air the yield is improved, likewise if the spray be formed from solutions of oxygen-carriers (manganese salts). The material of the electrodes also influences the reaction; the best results were obtained with carbon, the worst with platinum and with aluminum. Under favorable circumstances sixteen percent of the weight of the air passed through the apparatus may be converted into oxids of nitrogen. *W. L. M.*

The Dissociation of Chlorin Hydrate in Aqueous Solutions at Zero. *A. A. Jakowin. Ber. chem. Ges. Berlin,* **30,** *518 (1897).* Dissociation takes place according to the chemical equation $Cl_2aq \rightleftarrows (ClH + ClOH)aq$. The degree of dissociation was ascertained by measuring the electrical conductivity of the solution (ClOH is no electrolyte) and was confirmed by determining the distribution coefficient of the chlorin between the solution and carbon tetrachlorid. The author points out that two different formulas for the dissociation isotherm for this reaction are obtained according as the Arrhenius-van 't Hoff theory or the older form of the Guldberg-Waage equation is made the basis of the calculation. His results are in agreement with the former, whereas «the variations from the second formula reach 200 percent and more.» *W. L. M.*

The Action of Glowing Carbon on a Mixture of Chlorin and Steam. *A. Naumann and F. G. Mulford. Ber. chem. Ges. Berlin,* **30,** *347 (1897).* A current of chlorin, after passing through a vessel filled with water, was led into a porcelain tube filled with charcoal and heated in a combustion furnace. By varying the temperature of the water, the ratio between chlorin and steam could be regulated; the temperature of the furnace was ascertained by a thermoelectric couple, it varied from 414°C to 825°C in the different experiments.

The reaction takes place for the most part according to the equation

$$2Cl_2 + 2H_2O + C = 4HCl + CO_2.$$

Below 500°C a large proportion of the gases passes through the tube unacted upon; while high temperatures and long contact with the carbon reduce part of the CO_2 to CO, accumulation of this latter however is hindered by the subsidiary reaction—

$$Cl_2 + H_2O + CO = 2HCl + CO_2.$$

W. L. M.

Osmotic Pressure

The Theory of Solutions. *Lord Rayleigh. Nature*, **55**, *253* (*1897*). A careful proof of van 't Hoff's theorem that the osmotic pressure of a dilute solution of a gas is equal to the pressure which the substance would have as gas at the same temperature and density. The demonstration does not differ essentially from the original reasoning of van 't Hoff, and it considers only involatile solvents.

J. E. T.

Osmotic Pressure. *Lord Kelvin. Nature*, **55**, *272* (*1897*). It is remarked that the theorem presented by Rayleigh (see preceding review) is not useful as a guide for experiment, apparently because it vastly underestimates the osmotic pressure for common salt and other simple substances. Further, two components separated by a semipermeable wall and closed by pistons are supposed to contain two fluids, one on both sides and the other on but one; it is then stated that when these fluids are perfect gases the osmotic pressure is clearly the partial pressure of the second component, but when they are liquids we have no theoretical guide as to the pressure. All who are occupied with the theory of solutions are advised to take to heart the deliverances of Fitzgerald in his absurd Helmholtz Memorial Lecture. *J. E. T.*

Semi-Permeable Films and Osmotic Pressure. *J. W. Gibbs. Nature*, **55**, *461* (*1897*). To solve Lord Kelvin's problem concerning osmotic pressure (see preceding review) requires only the relation between density and pressure for the fluid when this relation for small densities become that of an ideal gas; in other cases a single constant in addition suffices. To show this for the case where the two fluids are gases Gibbs supposes each compartment extended vertically until the ideal states are reached. For each—

$$dp = -g\gamma dz$$

(the letters denoting pressure, gravity, density, height); integrating for each column, introducing, for the upper regions, $p = at/\gamma$ and the relation between densities and composition there, he finds

$$F(p_\alpha) - F(p_\beta) = at \log (1 + n),$$

where n is the number of molecular weights of solute per one of solvent in the column α, and the derivative of $F(p)$ is $1/\gamma$. When n is small the equation becomes van 't Hoff's law

$$p_\alpha - p_\beta = atn\gamma.$$

The same result is shown to hold when a nonvolatile solvent is assumed.

Let a mass of solution be separated by osmotic walls from pure solvent (1) and (gaseous) solute (2). With the latter distributed in the ratio $1/B$ between its two compartments its densities satisfy

$$\gamma_2''' = B\gamma_2''.$$

The potential of the (ideal) gas is

$$\mu_2''' = a_2 t \log \gamma_2''' + C,$$

whence

$$\mu_2'' = a_2 t \log (B\gamma_2'') + C \qquad \text{(I)}$$

(the constants B and C can be united). Equation (I) expresses van 't Hoff's law, for the general equation

$$vdp = \eta dt + m_1 d\mu_1 + m_2 d\mu_2$$

becomes

$$dp'' = \gamma_2'' d\mu_2''$$

or, substituting from (I), $dp'' = a_2 t d\gamma_2''$

whence integrating from $p'' = p'$ and $\gamma'' = 0$,

$$p'' - p' = a_2 t \gamma_2''$$

which is van 't Hoff's law. When the solute is not volatile the same result follows if mutually repulsive forces are ascribed to its «molecules».

J. E. T.

The Theory of Osmotic Pressure. *J. Larmor. Nature*, **55**, *545* (*1897*). Chiefly molecular-kinetic considerations which lead nowhere. The hypothesis of ionization, and van 't Hoff's law for the osmotic pressure of a dissolved gas, probably, in some form, hold the field; though basing the osmotic law on Henry's absorption law «hardly amounts to a physical demonstration because it only deduces one empirical relation from another».

J. E. T.

The Osmotic Properties of the Cells, and their Importance for Toxicology and Pharmacology. *E. Overton. Zeit. phys. Chem.* **22**, *189* (*1897*). After an introduction, in which he argues that the absorption and secretion of dissolved substances by living cells is in many cases not purely an osmotic process, the author gives a condensed account of the results of an extensive experimental investigation undertaken to solve one of the problems connected with the phenomenon of «selective absorption», viz: — Is there any difference between different animal and vegetable cells in respect to the permeability of their walls and protoplasm for substances in solution?

Two methods were employed, the first being a modification of de Vries's method of plasmolysis, and the second depending on the formation of insoluble compounds of the dissolved substances with the tannins found in certain cells. Several thousand experiments seem to place it beyond doubt that the permeability of the most various animal and vegetable cells (with possible exception of the fungi) is in all essentials the same, and that the power of any given substance to penetrate the protoplast depends on its chemical constitution alone.

Thus the cells are impermeable for all compounds which in moderately dilute solution are largely dissociated into ions. Among the others, the organic compounds may be classified according to the presence of certain groups in their structural formulas, whose presence prevents or at all events retards their entrance into the cell. The most important of these groups may be arranged in the following series, beginning with the most effective: 1, the amido acid group; 2, carboxyl; 3, amids; 4, alcoholic hydroxyl; 5, aldehydes; 6, (little or no effect) the keto, nitrile and lactone groups; also others (oxids); 7, (no retarding effect) the halogens. All alkaloids investigated pass quickly through the walls. If several «retarding groups» are present in the same compound the effect is much increased. *W. L. M.*

An Apparatus for studying the Laws of Filtration and Osmosis of Liquids in Motion. *H. J. Hamburger. Arch. néerl.* **30**, *353* (*1896*). The apparatus consists of an outer metallic tube surrounding an inner concentric tube of wire gauze, on which is supported a film of gelatin or collodion. The liquids to be experimented on flow through the inner tube and through the annular space between the inner and outer tubes, respectively; by means of two manometers and a system of taps and movable reservoirs the pressures in the two tubes and the rates at which the liquids pass through them can be regulated.

Preliminary experiments by the author lead him to the conclusion that the greater the rate at which the liquid passes through the inner tube, the greater will be the quantity of liquid that diffuses into it through the membrane.

«The gelatin tube and the annular space are both filled with the *same* blood serum . . . the more rapidly the liquid flows through the central tube the more rapidly does the liquid diminish in the annular space. In the case of a liquid in circulation the diminution may amount to ten times that observed in the case of a simple difference of pressure.»

No details are given, nor does the author suggest any explanation save that «in my opinion it is a simple mechanical process»; he contents himself with pointing out the importance of his discovery for the elucidation of certain physiological problems. *W. L. M.*

On the Diffusion of Metals. *W. C. Roberts-Austen. Phil. Trans.* 187 (A), *383* (*1896*). The author has determined the rates of diffusion of gold, platinum and rhodium in melted lead; of gold in melted bismuth; of gold, silver and lead in melted tin. The measurements agree very well with the formula of Fick. Gold was found to diffuse at a measurable rate into solid lead. At 250° the constant is 0.03 as against 3.0 in melted lead at 500°. At 800° gold diffuses into solid silver at much the same rate as into lead at 200°. It would seem as if diffusion of one solid into another could take place only when a solid solution was formed; but it is conceivable that surface tension phenomena might complicate the problem. The reviewer would suggest that tin and gold would probably behave very differently in contact with solid lead. *W. D. B.*

Note on Computing Diffusion. *G. F. Becker. Am. Jour. Sci.* (*4*) 3, *280* (*1897*). The author points out that when the diffusing quality at the initial plane is kept constant and the space into which it diffuses may be regarded as infinite, the quality at any distance measured perpendicularly to the initial plane is then proportional to the area of the «probability curve» taken between certain limits. Since this area has been computed and tabulated the problem becomes a very simple one. The author also calls attention to the fact that it would be of great assistance to geologists if they could assume that the formula $k\mu_{,} = const$ applies to rock magmas—k being the diffusion constant and μ the coefficient of viscosity.

W. D. B.

The Coefficients of Elasticity and Wave Motion as Functions of Molecular Weight and Specific Heat. *O. Foerster. Zeit. für Math. und Phys.* **41**, *258* (*1897*). Wertheim found that

$$E(M/D)^{1/3} = constant$$

for all metals, E denoting the coefficient of elasticity, M the molecular volume and D the density. With employment of atomic hypotheses concerning the forces requisite to separate molecules, the relation of the moments of molecules to their masses, etc., it is concluded that $E = (77.33Dc)^{1/3}$ should hold true,—c denoting the specific heat. Values calculated from the formula agree only approximately with Wertheim's experimental data. *R. B. W.*

Velocities

Velocity of the Reaction between Ferrous Chloride, Potassium Chlorate and Hydrochloric Acid. *A. A. Noyes and R. S. Wason. Jour. Am. Chem. Soc.* **19**, *199*; *Zeit. phys. Chem.* **22**, *210* (*1897*.) Measured quantities of the solutions of ferrous chlorid and hydrochloric acid were mixed in stoppered bottles, warmed to 20°C in a thermostat, and then the potassium chlorate solution added from a pipette. At suitable intervals portions of 25–50 cc were removed and titrated with permanganate.

The rate of change was found proportional to the concentration of each of the three substances reacting; a comparison of the constants of several series of experiments with different initial concentrations also gives evidence that the reaction is of the third order.

The influence of the temperature on the velocity may be expressed by van 't Hoff's formula. A rise of 10°C causes the constant to increase in the proportion of 1 : 2.2–2.7. *W. L. M.*

Dynamic Investigation of the Formation of the Azo Dyes. *H. Goldschmidt and A. Merz. Ber. chem. Ges. Berlin*, **30**, *670* (*1897*).

1. *Methyl orange* from dimethylanilin hydrochlorid and *p*-diazobenzene sulfonate of sodium at 20°C. The amount of diazo compound unaltered was estimated by measuring the nitrogen evolved on boiling the solution. The rate of the reaction may be represented by a formula deduced from the assumption that the velocity is proportional to the concentration of the diazo acid and to that of the hydrolytically dissociated part of the aniline salt.

2. The reaction of 0°C of *p*-diazobenzene sulfonate of sodium on alkaline solutions of *m*- and *p*-cresol. On developing equations based on the assumption that the velocity is proportional to the hydrolytically dissociated portions of the phenates and sulfonates, they yield the remarkable result that the *time* occupied by the reaction is proportional to the concentrations of the phenol and of the diazo sulfonate; the experiments quoted fully confirm this relation, which is the exact opposite of that in the ordinary bimolecular reaction! *W. L. M.*

On the Velocity of Formation and Decomposition of Ethers. *O. Knoblauch. Zeit. phys. Chem.* **22**, *268* (*1897*). Measurements from both ends of a reversible reaction should, according to the theory, give the same pair of values for the velocity constants. The author tests this on the reaction $CH_3CO_2H + C_2H_5OH \rightleftharpoons CH_3CO_2C_2H_5 + H_2O$ and finds the prediction of theory confirmed. Hitherto measurements have been made only on the formation of esters. In order that the conditions might be the same in both cases HCl was used as a catalyzer (eliminating the action of the H-ions of the CH_3CO_2H) and the medium was in both cases a quantity of $H_2O + C_2H_5OH$ large enough to be appreciably constant in concentration throughout the reaction. The temperature was 25°. *E. B.*

On the Decomposition of Hydriodic Acid by Light. *M. Bodenstein. Zeit. phys. Chem.* **22**, *23* (*1897*). Experiments with HI at various concentrations show that the decomposing action of sunlight follows the monomolecular scheme H + I = HI instead of the bimolecular scheme which represents the reaction in the dark at high temperatures (see above, page 601). The temperatures were the ordinary summer temperatures of Heidelberg. *E. B.*

The Speed of Reduction of Chromic Acid by Phosphorous Acid. *G. Viard. Comptes rendus*, **124**, *148; Bull. Soc. Chim. Paris*, **17**, *213* (*1897*). The reaction $4CrO_3 + 3P_2O_3 = 2Cr_2O_3.3P_2O_5$, was followed, at 0°C, with varying conditions of concentration. Titrations of residual chromic acid were made with ammonium ferrous sulfate in acid solution, at intervals of one or more days. Even with maximum concentration only 78.3 percent of the chromic acid was reduced in sixty days. Up to about 60 percent the speed varies approximately as the fourth power of the active mass; yet the equation

$$dx/dt = K(A - x)^4$$

must be regarded as an empirical formula merely; for in the several series, the calculated values of K are found to rise to a maximum and then to diminish. The initial coefficient of speed, as determined by graphical extrapolation, varies nearly as the 1.4 power of the concentration. These facts indicate an important hindering influence, as the reaction proceeds, which may prove an inviting field for further study. *R. B. W.*

Drying and Deliquescence of Certain Salts. *F. W. Smither. Am. Chem. Jour.* **19**, *227* (*1897*). The author has determined the rate at which various salts take up water. He seems not to know that all salts will take up an infinite amount of water in presence of saturated water vapor. Since most of the measurements were made after saturated solutions were formed they have little or no value. *W. D. B.*

On the Rate of Crystallization. *G. Tammann. Reprint* (*1897*). The rates of crystallization of a number of supercooled liquids were found to be proportional to the amount of supercooling down to fifteen degrees below the freezing point. From fifteen to thirty degrees the rate was independent of the degree of supercooling. On carrying the supercooling still farther there should come a point where the heat evolved will not raise the solid to its melting point and the reaction velocity will decrease. With benzophenone at − 40° it was found that the reaction velocity was apparently zero. At − 35° crystallization took place, though very slowly. The author calculated that with supercooled phosphorus the rate of crystallization must decrease as the temperature falls below + 18° and found experimentally that the rate at 24° was roughly one hundred times that at 0°. *W. D. B.*

A Further Study of the Birotation of Glucose. *H. Trey. Zeit. phys. Chem.* **22**, *424* (*1897*). A very interesting paper which brings up a large number of puzzling problems. It is to be hoped that in a future paper the author may be able to settle some of the points raised. The complexity of the subject is such as to make this possibly a vain hope. We do not know definitely to what the birotation of glucose is due. We have some sort of decomposition taking place with alkalies and with acids. We have the nature of the solvent coming in and complications due to the presence of neutral salts. Altogether it is not a pleasing outlook and the author will deserve great credit if he succeeds in straightening out this subject. *W. D.B.*

On the Ratio between Inversion Velocity and Concentration of Hydrogen as Ion. *W. Palmaer. Zeit. phys. Chem.* **22**, *492* (*1897*). Measurements were made with extra pure sugar in platinum vessels. The author noticed that with dilute acids there is a birotation of the invert sugar. The final measurements showed that the ratio of the reaction velocity constant to the concentration of hydrogen as ion is constant when the concentration of the acid does not exceed one-hundredth normal. For tenth-normal acid this is no longer true. *W. D. B.*

On the Diazotizing of Anilin. *Niementowski and Roskowski. Zeit. phys. Chem.* **22**, *145* (*1897*). Reviewed in this Journal **1**, 324, from Bull. Acad. Cracovie.

Electromotive Forces

Magnetization of Liquids. *J. S. Townsend. Phil. Trans.* **187** (A), *533* (*1896*). A full account of measurements of the coefficients of magnetization k of solid and dissolved iron salts and the theory of the method, partly reported in the Proc. Roy. Soc. and reviewed in this Journal **1**, 271. It is added that free sulfuric acid in the sulfate solutions does not alter k, nor does k vary on neutralizing the acid with potassium hydroxid; precipitating with hydroxid, however, increases k. The solid salts have nearly or quite the same k as their solutions. When iron is not present as ion, as in potassium ferrocyanid or ferricyanid, k has the same value as for pure water. The k falls rapidly with rising temperature, according to the formula $k = k_0(1 - \alpha t)$, where α depends upon the temperature but not upon the anion; k for the solvent is independent of the temperature. Alcoholic and aqueous solutions have the same temperature coefficient. *J. E. T*

On the Chemical Equilibrium, Electromotive Activity and Electrolytic Separation of Metallic Mixtures. *W. Nernst. Zeit. phys. Chem.* **22**, *539*, (*1897*). For equilibrium the author derives the formula $\sqrt[n_1]{\frac{P_1}{p_1}} = \sqrt[n_2]{\frac{P_2}{p_2}}$ where P_1 and P_2 are the solution pressures, p_1 and p_2 the osmotic pressures, n_1 and n_2 the valences of the two metals. If the two metals form a solid solution, this equation is identical with that obtained by Ogg, only that here the theoretical inaccuracy of assuming that the solution pressure is unchanged becomes more evident.

If the two metals do not form a solid solution we have for the potential difference at the electrode

$$F = \nu \frac{RT}{n_1} \log \frac{P_1}{p_1} + (1 - \nu) \frac{RT}{n_2} \log \frac{P_1}{p_2}$$

where ν is the percentage of the quantity of electricity which passes into solution with the first metal. For equilibrium this goes over into

$$F = \frac{RT}{n_1} \log \frac{P_1}{p_1} = \frac{RT}{n_2} \log \frac{P_2}{p_2}$$

For electrolytic precipitation by zero current, on the assumption that chemical equilibrium obtains at each moment, the author writes the equation—

$$\delta \sqrt[n_1]{\frac{P_1}{p_1}} \cdot \sqrt[n_2]{\frac{p_2}{P_2}} = 0 .$$

The author regards this assumption as being almost certainly correct. The recent experiments of Ostwald and of Stortenbeker would seem to make this conclusion somewhat doubtful. *W. D. B.*

Electromotive Force and Distribution Equilibrium. Comments on Luther's Reply. *A. H. Bucherer. Zeit. phys. Chem.* **22,** *590* (*1897*). Among other things the author still insists that the dissociation theory assumes the existence of hydrogen and hydroxyl as ions in water vapor. He also attributes to Nernst, page 595, the idea that in equilibrium the concentrations of a substance in two non-miscible liquids are identical. The other points in the paper are questions of priority. *W. D. B.*

Investigations of the Processes in the Carbon Cell. *C. Liebenow and L. Strasser. Zeit. Elektrochemie,* **3,** *353* (*1897*). Iron is at first attacked by caustic potash and then changes suddenly into a passive state. This passive state is brought about more quickly by air or an oxidizing agent and is destroyed by a reducing agent. The same phenomenon was noticed with nickel and with silver. The Jacques cell is therefore carbon, caustic potash, passive iron as was first pointed out by the reviewer, this Journal **1,** 322 (1897).

W. D. B.

On the Change of the Free Energy by the Formation of Insoluble Mercury Compounds. *S. Bugarszky. Zeit. anorg. Chem.* **14,** *145* (*1897*). The author has determined the electromotive forces of cells with insoluble mercury salts as depolarizers and the temperature coefficients of the cells. The comparison of the results with the thermochemical data of Varet is not very satisfactory, since the error is less than two percent in only two cases out of ten. *W. D. B.*

On the Internal Resistance of Galvanic Cells and especially of Accumulators. *E. Haagn. Zeit. Elektrochemie,* **3,** *421* (*1897*). A preliminary notice of a paper to be published in the *Zeitschrift für physikalische Chemie.* *W. D. B.*

The Electrical Resistivity of Electrolytic Bismuth at Low Temperatures and in Magnetic Fields. *J. Dewar. Proc. Roy. Soc.* **60**, *425* (*1897*). Measurements of the resistance at + 19°C, — 79°C, — 185°C and — 203°C of a wire 0.5245 mm in diameter, placed transversely to the direction of the field of an electromagnet, while the field varied from zero to nearly 22000 c.g.s. units. The paper is illustrated by three curves showing «how remarkably the resistance is effected by magnetization. The curve of resistance taken in liquid air, — 182°C, shows that by a transverse magnetizing field having a strength of 22000 c.g.s. units the resistance of the bismuth is made 150 times greater than the resistance of the same wire in a zero field but at the same temperature; the lower the temperature to which the bismuth is reduced the greater is the multiplying power of a given transverse field upon its electrical resistivity». Extrapolation shows that at a temperature of + 150°C the conductivity would probably cease to be affected by the field. «In this respect bismuth is a remarkable exception to other metals. We have tried the effect of transverse magnetization at low temperatures on zinc, iron and nickel but find no effect sensibly greater at low than at high temperatures, although these metals have their resistance affected by magnetization to a small degree». *W. L. M.*

Electrolysis and Electrolytic Dissociation

Relations between the Affinity Constants and the Chemical Constitutions of Organic Acids. *B. Szyszkowski. Zeit. phys. Chem.* **22**, *173* (*1897*). Measurements at 25°C of the conductivities of nineteen organic acids, of which fourteen are oxyacids. The electrical dissociation constants of the tertiary β-oxyacids are on the average twice as great as are those of the secondary β-oxyacids with approximately the same empirical composition. The author finds it almost impossible to decide whether the methyl group or the hydrogen atom is the more ‹positive›; the methyl group is on the whole more ‹negative› than its homologues; residues with the iso-structure are more negative than the isomeric ‹normal› groups.

From a table of the constants for nineteen unsaturated and ten saturated acids it appears that in every case the acid whose formula contains a treble bond is far stronger than the acid formed from it by addition of two atoms of hydrogen, and this again than the corresponding saturated acid. *W. L. M.*

The Temperature and Ohmic Resistance of Gases during the Oscillatory Electric Discharge. *J. Trowbridge and T. W. Richards. Am. Jour. Sci.* [*4*] **3**, *327* ; *Phil. Mag.* [*5*] **43**, *349* (*1897*). An apparent resistance of hundreds of thousands of ohms in the Plücker tube (as observed under a continuous current of about one milliampere) is broken down by the spark of a large condenser to five or six ohms. To establish a method for measuring resistances under such conditions, many photographs were taken (with the aid of a Fedderson revolving mirror) of the discharge from one, two or three large Leyden jars, damped by a variable resistance. By tabulating the results, the number of half oscillations, with a given capacity of condenser, could be used to estimate the resistance of the circuit. By the use of this new method, with Plücker tube, the following conclusions were reached :—

1, The resistance of a gas at low pressure to the oscillatory discharge is equivalent to only a very small ohmic resistance; 2, this resistance is in general greater the less the quantity of electricity ; 3, down to a very small pressure, this resistance decreases with the tension of the gas; 4, the form of the tube has an important effect upon the resistance of the gas; 5, with the oscillatory discharge, it is evident that the electrodes produce far less effect than with the continuous discharge.

Since the spark seems to pass in about one millionth of a second, a very usual discharge would represent a current of 100 amperes for this space of time, representing a very high temperature. The resulting dissociation may easily account for the difference between the spectrum observed with condenser, and that obtained by continuous discharge. *R. B. W.*

Does a Vacuum conduct Electricity ? *J. Trowbridge. Am. Jour. Sci.* [*4*] **3**, *343* ; **The Electric Conductivity of the Ether.** *Same* **3**, *387* ; *Phil. Mag.* [*5*] **43**, *378* (*1897*). The author's experiments lead him to conclude that a disruptive discharge of electricity encounters its chief resistance at the surface of the electrodes, with very little resistance during the discharge in a rarefied medium. The resistance of a Crookes tube, to the disruptive discharge, seems to diminish, the nearer we approach a vacuum. Ohm's law does not hold for electric sparks in air or gases. The author concludes that under very high electrical stress the ether breaks down and becomes a good conductor. *R. B. W.*

The Effect of Great Current Strength on the Conductivity of Electrolytes. *T. W. Richards and J. Trowbridge. Am. Jour. Sci.* [*4*] **3**, *391* ; *Phil. Mag.* [*5*] **43**, *376* (*1897*). The resistances of copper, zinc and cadmium sulfates, to the oscillatory discharge from one or more Leyden jars, were tested by the damping effect, as described in the paper reviewed above. The resistances thus found agreed with those obtained by the method of Kohlrausch, showing that the conductivity of electrolytes is not essentially affected by great changes of current strength. The great heat capacity of the solutions as compared with gases may account for this difference in behavior.

R. B. W.

On the Law of Thermal Constants. *D. Tommasi. Bull. Soc. Chim. Paris,* (*3*) **17**, *438* ; *Elektrochem. Zeit.* **4**, *28* (*1897*). The author complains that he is not given credit for the law advanced by him in 1882, reading as follows: « If one metal replaces another in a salt solution, the number of calories set free is the same for each metal, irrespective of the nature of the acid. » The author claims also that the law is absolute, whereas it applies strictly only to cases in which there is complete electrolytic dissociation. *W. D. B.*

Laboratory Apparatus for Electrolysis with Stationary and Flowing Solutions. *H. Wehrlin. Zeit. Elektrochemie,* **3**, *450* (*1897*). The apparatus consists of a tube having holes in it for the usual purposes. The electrodes close the ends of the tube. The author does not explain in what respect this piece of apparatus is an improvement over others already in the market. *W. D. B.*

The Electrochemical Equivalent of Carbon. *A. Coehn. Zeit. Elektrochemie,* **3**, *424* (*1897*). A series of experiments upon the electrolysis of sulfuric acid with a carbon anode shows that the loss in weight corresponds to a value of three for the electrochemical equivalent of carbon. *W. D. B.*

On the Preparation and Properties of Potassium Percarbonate. *A. v. Hansen. Zeit. Elektrochemie,* 3, *445* (*1897*). The three essentials are low temperature, concentrated solution and high current density. The authors recommend the salt as a means of procuring oxygen, one hundred grams yielding about five liters of oxygen. *W. D. B.*

On the Chemical Decomposition of Sulfur. *T. Gross. Elektrochem. Zeit.* 4, *1* (*1897*). By electrolysis of fused silver chlorid and sulfid the author claims to have obtained a new element «bythium» by decomposition of sulfur. Instead of studying the properties of this new element, he sets himself the more inspiring task of decomposing the halogens, beginning with chlorin. *W. D. B.*

A New Electrolytic Hypothesis with Reference to the Manufacture of Chlorates. *J. Hargreaves. Electrochem. Zeit.* 4, *15* (*1897*). The idea in this somewhat mysterious paper seems to be that the anion is a by-product formed by the cation striking the anode because changing the conditions of electrolysis alters the amount of chlorate formed. The reviewer is not sure how this conclusion was reached but he was puzzled at the outset by the statement that oxygen is the only anion which can appear at the cathode under the circumstances. *W. D. B.*

On Mixed Haloid Platinates. *A. Miolati. Zeit. anorg. Chem.* 14, *237* (*1897*). In order to determine whether there is a compound $K_2PtCl_4Br_2$ the author measured the conductivity of a solution made from crystals having this composition and also of a solution containing two of K_2PtCl_6 and one of K_2PtBr_6. In both cases the conductivity increased on standing; but the maximum conductivity is not the same in the two cases. The salt K_2PtCl_6 in solution does not change but K_2PtBr_6 does. Under the circumstances no conclusions were drawn. *W. D. B*

Electrical Discharges in Electrolytes. *P. Cardani. Nuovo Cimento,* (*4*) 4, *200* (*1896*). The author finds that the resistance of an electrolyte to discharges from a condenser follows the laws for galvanic currents, the theory of discharges through metallic conductors not being applicable. *W. D. B.*

On the Electrical Resistance of Salt Solutions in Motion. *I. Bosi. Nuovo Cimento,* (*4*) **5**, *249* (*1897*). The author finds experimentally that when the solution moves in the same direction as the current the resistance is increased if the cation has a higher migration velocity than the anion and is reduced if the contrary be true. If the solution and current move in opposite directions, the resistance increases if the anion has a higher migration velocity than the cation and diminishes if the reverse be the case. The increase in the resistance is always greater than the decrease caused by reversing the direction of flow. When anion and cation have the same migration velocity, the effect due to the motion of the solution is zero; though potassium chlorid would have been a better example of this than potassium sulfate. The theoretical treatment of the subject is entirely unsatisfactory, owing to the author's assumption that Hittorf's views on electrolysis are incompatible with the electrolytic dissociation theory. *W. D. B.*

On the Number of Ions in Some Cobalt-Ammonia Compounds. *E. Petersen. Zeit. phys. Chem.* **22**, *410* (*1897*). The author has made determinations of the freezing points and conductivities of dilute solutions of cobalt-ammonia compounds. The conclusions to be drawn from these results do not harmonize with those reached by Jörgensen. The author therefore says in a despairing manner that the conductivity is entirely useless as a means of determining the constitution of a solid compound. *W. D. B.*

On the Measurement of High Electrolytic Resistances with Direct Current. *R. Malmström. Zeit. phys. Chem.* **22**, *331* (*1897*). The author has made a direct comparison of Kohlrausch's method with that of Nernst, Zeit. phys. Chem. **14**, 642 (1894), and finds that the latter gives excellent results. *W. D. B.*

Experimental Study of Electrolytic Iron. *L. Houllevigue. Jour. de Phys.* (*3*) **6**, *246* (*1897*). The amount of hydrogen in electrolytic iron increases with the current density and with the amount of ammonium chlorid in the bath. The author has studied the properties of an iron containing 16.3 cc hydrogen per gram of iron and finds that they resemble in a remarkable manner those of a cast iron in which the hydrogen is replaced by an equivalent quantity of carbon. *W. D. B.*

On the Transference Number of the Chlorin in Hydrochloric Acid in Different Solvents. *C. Cattaneo. Rend. Accad. Lincei,* (*5*) **6,** *279* (*1897*). The transference number for chlorin in hydrochloric acid seems to be about 0.21 when the solvent is water, ethyl alcohol, ethyl ether or chloroform, and about 0.24 for methyl alcohol, amyl alcohol or glycerol. Owing to the great experimental difficulties, the author is inclined to look upon these numbers as identical. Copper and gold were taken as anodes. The temperature to which the experiments refer is not mentioned. *W. D. B.*

On an Apparatus for Determining the Thermal Conductivity of Poor Conductors. *E. Oddone. Rend. Accad. Lincei,* (*5*) **6,** *286* (*1897*). The apparatus is essentially that proposed by Venske, and the author describes in detail the method and the corrections to be applied. He finds no difficulty in making measurements accurate to within five percent and hopes to reduce the possible error still farther. *W. D. B.*

On the Theory of Electrolytic Dissociation in Solvents other than Water. II, Acetone. *G. Carrara. Gazz. chim. Ital.* **27,** *I, 207* (*1897*). In the first paper of the series, Gazz. chim. Ital. **26,** I, 119 (1896), the author studied the conductivity of substances when dissolved in methyl alcohol. We now have measurements on LiCl, KI, NaI, NH_4I, $N(CH_3)_4I$, $(CH_3)_3SI$, $(C_2H_5)_3SI$, CCl_3COOH and HCl in acetone. With the inorganic salts the increase of the conductivity is much greater than with water as solvent and the maximum approached is higher. On the other hand hydrochloric and trichloracetic acids are almost non-conductors. *W. D. B.*

Solution and Pseudo-solution. III, The Electrical Convection of Certain Dissolved Substances. *H. Picton and S. E. Linder. Jour. Chem. Soc.* **71,** *568* (*1897*). When the solutions conduct slightly there is visible repulsion of the colloid matter from one of the electrodes. If no current passes no effect can be detected, even when the potential difference between the electrodes is over two hundred volts. The authors are not yet able to predict from which electrode any given substance will be repelled. It is easier to drive the coarser colloids downwards than upwards, doubtless owing to the influence of gravity. *W. D. B.*

On the Constitution of Inorganic Compounds, III. *A. Werner and A. Miolati. Zeit. phys. Chem.* **21**, *225* (*1896*) ; *also* **12**, *35* (*1893*) *and* **16**, *506* (*1895*). *Gazz. chim. Ital.* **27**, *I*, *299*. In a paper with the same title, Zeit. anorg. Chem. **3**, 267 (1893), Werner has elaborated a theory of the constitutions of double salts, metal ammonia compounds, hydrates, etc., and of the conditions of their electrolytic dissociation in aqueous solution. In the three papers referred to above the authors have published measurements of the conductivities of about fifty different cobalt-ammonia salts and have found « in every case satisfactory correspondence between the results of experiment and the requirements of the theory. » *W. L. M.*

Electrical Conductivity of Diethylammonium Chloride in Aqueous Alcohol. *J. Walker and F. J. Hambly. Jour. Chem. Soc.* **71**, *61* (*1897*). An investigation to determine the effect of alcohol in reducing the degree of dissociation of the solute and the speed of the ions. Diethylammonium chlorid was used in pure water, in 99 percent alcohol, and in mixtures of these solvents. From the curves it is apparent that the water and the alcohol have analogous actions on the salt.

Whatever the composition of the solvent, μ increases on dilution, but in pure water and in 99 percent alcohol, μ increases more rapidly for equal dilution than in mixtures of these solvents. μ is smallest in 99 percent alcohol and rises with the percentage of water.

The percentage dissociation, $100(\mu_v/\mu_\infty)$, increases much more rapidly in 99 percent alcohol on dilution than in pure water or in mixtures of these solvents. In a set of curves connecting μ and the percentage of alcohol, the two effects of alcohol, namely, in reducing the dissociation and the speed of the ions, are separately seen.

C. L. S.

Note on the Variation of the Dissociation Coefficient with Temperature. *S. R. Milner. Phil. Mag.* [*5*] **43**, *286* (*1897*). With a Carnot cycle, wherein a dissolved electrolyte is expanded at the temperature T and compressed at $T - dT$ against a semipermeable piston, the degree of ionization varying with the varying volume of the solution, the author calculates the rate of change of ionization with changing temperature. He finds separately the work of expansion for the undissociated substance and that for the ions, using the Ostwald mass law formula $Kc = c'^2$ and the equation $c + c' = C$ for the integration; he then applies these relations to transform the results into terms of the initial and final total concentrations, and adds to get the total work W.

The heat H absorbed in dissociation during expansion is the dissociation times the heat Q absorbed in dissociating one molecular weight, which with the aid of the same general relations is expressed by K, the total concentrations and Q. Equating the total work of the cycle with the fraction dT/T of the total heat $W + JH$, and reducing, yields the van 't Hoff formula $\partial \log K/\partial T = Q/RT^2$.

J. E. T.

On the Molecular Conductivity of Salts in Solution. *P. Joubin. Jour. de Phys.* (*3*) **6**, *180* (*1897*). Essentially a reprint, from the *Comptes rendus*, of a paper reviewed in this Journal **1**, 524, together with the appended remark that for the author's conclusions it is necessary that the temperature coefficient of the dielectric constant have the same value for both the solution and the pure solvent.

J. E. T.

An Effective and Convenient Way to Purify Water. *H. C. Jones and E. Mackay. Zeit. phys. chem.* **22**, *237* (*1897*). Steam from ordinary distilled water containing $KMnO_4$ and H_2SO_4 is passed into the water whose vapor is to be condensed. This water is in an ordinary retort and contains $KMnO_4$ with NaOH. The vapor is condensed in the usual way in a block tin condenser. Asbestos is used for joints, instead of cork or rubber. Conductivity of water so purified $= 1.5$ to 2.0×10^{-6} mercury units. Compare Hulett, this Journal **1**, 91 (1896).

J. E. T.

Structure Phenomena

Ultraviolet Spark-Spectra of Certain Metals. *F. Exner and E. Haschek. Sitzungsber. Akad. Wiss. Wien*, **104** (*IIA*) *909*; **105**, (*IIA*) *389, 503, 707* (*1897*). Photographic measurements of the spark spectra of the following elements: Ag, Cu, Mn, Wo, Mo, Pt, Pd, Ir, Rh (Ru and Os page 707 *ff*). The current from a Tesla transformer

(10,000 volts) produced a spark 3-4 mm long between electrodes 8-10 mm in length and 2-3 mm in breadth. The light, after concentration by a quartz lens, passed through a slit in a sheet of tin-foil on a quartz plate and was analyzed by a Rowland's grating: the apparatus was so arranged that a photograph of the iron spectrum was taken on the same plate with each of the others. When completed the photographs were projected on a screen provided with a scale; by means of Rowland's normal lines and Kayser and Runge's tables of the wave lengths of the lines in the iron spectrum, the image was adjusted to its correct position on the scale, and the wave lengths and approximate brightness of the various lines were read off. The probable error is set at somewhat less than one tenth Ångström unit.

After publication of the first paper, the authors became possessed of an improved grating, and the second and third papers contain, beside reproductions of the photographs, merely addenda and corrigenda to the first. The fourth paper is devoted to ruthenium and osmium. *W. L. M.*

On the Indices of Refraction of the Blue and Green Solutions of Chrome Alums. *C. Soret, A. Borel and E. Dumont. Arch. de Genève* (4) **3**, *376* (*1897*). Measurements were made with ammonium chrome alum and with potassium chrome alum. The blue solutions have a higher index of refraction than the green solutions. From the experiments it is impossible to tell whether this difference (about 0.00047) is or is not a function of temperature and concentration.
W. D. B.

Spectrochemistry of Nitrogen. V. *J. W. Brühl. Zeit. phys. Chem.* **22**, *373* (*1897*). The author has recorded in this paper the optical constants of ninety-five substances containing nitrogen.
W. D. B.

On the Refractive Index of Mixtures of Two Liquids. *F. Zecchini. Gazz. chim. Ital.* **27**, *I*, *358* (*1897*). From the author's measurements it seems clear that the percentage composition of a mixture can not in general be calculated with great accuracy when only the indices of refraction of the mixture and of the pure components are known. *W. D. B.*

On Some Chromatic Reactions produced with Organic Acids, chiefly Tartaric, Citric and Malic Acids. *E. Piñerua, Gazz. chim. Ital.* **27**, *I, 195 ; Comptes rendus,* **124**, *291 (1897)*. On adding a fresh solution of β-naphthol in concentrated sulfuric acid to solutions of organic acids intense colors are obtained which change on addition of water. Nitrates, nitrites and chlorates also give marked colors when added to a solution of resorcin in sulfuric acid. *W. D. B.*

On the Absorption Spectra of Several Colorless Organic Compounds and their Relations to the Molecular Structure. *W. Spring. Bull. Acad. roy. Belg. (3)* **33**, *165 ; Recueil Trav. Pays-Bas,* **16**, *1 (1897)*. From a study of fifty-one compounds the author concludes that organic liquids are yellowish when they contain no hydroxyl group and bluish when they do. The thickness of the liquid layer varied from four to fifteen meters. *W. D. B.*

Position-isomerism and Optical Activity; the Comparative Rotatory Powers of the Dibenzoyl and Ditoluyltartrates. *P. Frankland and F. M. Wharton. Jour. Chem. Soc.* **69**, *1583 (1896)*. A continuation of a previous investigation, this Journal **1**, 196, in which Guye's theory is still further confirmed with these two classes of ethereal salts. *C. L. S.*

Preliminary Note on the Broadening of the Sodium Lines by Intense Magnetic Fields. *A. S. Dunstan, M. E. Rice and C. A. Kraus. Am. Jour. Sci. [4]* **3**, *472 (1897)*. Using Michelson's interferometer the authors have confirmed the recent observation of Zeeman, that the sodium spectral lines are broadened by the influence of a magnetic field. For fields from 0 to 7800 c.g.s. units the percentage broadening is stated to be proportional to the field strength. *J. E. T.*

The Optical Rotation of Aspartic Acid in Aqueous Solution. *E. P. Cook. Ber. chem. Ges. Berlin,* **30**, *294 (1897)*. At low temperatures (from 20°C up) the acid is dextrorotatory, at 75°C inactive, and above this temperature (to 90°C) laevorotatory. If to the solution of aspartic acid there be added hydrochloric or sulfuric acids the dextrorotatory power is much increased ; addition of alkalies (soda, ammonia) on the other hand, even in small quantity, changes the sign of the rotation.

The author suggests that these relations may be accounted for by assuming that the ion $C_4H_5NO_4$ is laevorotatory while the undissociated acid is dextrorotatory. *W. L. M.*

A New Formula for the Wave-Lengths of Spectral Lines. *J. J. Balmer. Verh. naturforsch. Ges. Basel,* **11**, *Heft 3; Astrophys. Jour.* **5**, *197* (*1897*). This investigation was prompted by a desire to replace the formula of Kayser and Runge

$$1/\lambda_n = A - B/n^2 - C/n^4$$

for the wave-lengths of the lines in the spark spectra of elements other than hydrogen, by a closed function of which the former might be a development in series. Formulating an accidentally noticed relation among the differences of the wave-lengths in any given series he obtains

$$\lambda_n = a \frac{(n+c)^2}{(n+c)^2 - b}$$

or

$$1/\lambda_n = A - B/(n+c)^2 \ .$$

Here a denotes the limiting wave-length in which the series of lines terminates; c denotes the displacement of the integral values of n, it is a constant fraction for each series; and b, when divided into a, gives a number closely equal to the corresponding quotient for the simple series of the hydrogen spectrum. Tested for lithium and helium the formula held good with an average variation of only about one-fourth of a unit. The accepted hydrogen formula is a special form of this one, obtained by setting $b = 4$ and $c = 0$. This formula closely resembles one proposed by Rydberg several years ago. Discussion of a diagram ot wave-lengths plotted against n as argument closes the paper. *J. E. T.*

Note on a Cause for the Shift of Spectral Lines. *G. F. Fitzgerald. Astrophys. Jour.* **5**, *210* (*1897*). When a body emits electromagnetic radiation the vibration frequency depends upon the specific inductive capacity of the surrounding medium. The oscillations of an electromagnetic oscillator can be calculated from $N^{-2} \alpha LC$, where L is self-induction and C is capacity. If the medium have a high specific inductive capacity C will be large and N will be small. An increase in the pressure of a gas increases the specific inductive capacity and so must alter the period of vibration of the molecules in it, if this period of vibration depends at all upon electric forces due to constant charges. Here is a true cause for some shift towards the red in luminous molecules. *J. E. T.*

On the Spectrum of Hydrogen. *H. Kayser. Astrophys. Jour.* **5**, *243* (*1897*). For the following reasons two series of lines in the spectrum of hydrogen must be assumed :—1, analogy with all the other elements, which have two series ending at the same point ; 2, the different appearance of the lines of the two series ; 3, the different conditions under which they appear ; 4, the second constant of the Kayser and Runge formula can have the same value for hydrogen as for all the other elements only when two series are assumed. *J. E. T.*

On Certain Emission Spectra of Cadmium, Zinc and the Haloid Compounds of Mercury and of Certain Other Metals. *A. C. Jones. Erlangen Dissertation, Leipzig, 1896* (*Barth.*) Observations of band spectra, the results being presented in drawings and tables. The bands were often made up of single lines, which in some cases were found to be arranged in pairs. *J. E. T.*

On the Electrification of Gases exposed to Röntgen Rays, and the Absorption of Röntgen Radiation by Gases and Vapours. *E. Rutherford. Phil. Mag.* [*5*] **43**, *241* (*1897*). Following up the work of Thomson and Rutherford, this Journal **1**, 323, the author studies the electrification of gases by the x-rays, and the properties of the charged gases. The chief observations having physicochemical interest relate to absorption of the radiant energy by gases and vapors. It is shown that good conductors under the x-rays are good absorbers of the radiation,—the absorbing powers have the relative order of the conductivities. The absorption does not seem to depend upon the molecular weight of the gas. Vapors like mercury and methyl iodid allow light to pass freely, but are very opaque to x-rays. In an appended note J. J. Thomson advances an interesting mode of expressing the connection between coefficient of absorption and the saturation current through the gas. *J. E. T.*

Notice on Poynting's Theorem. *P. S. Wedell-Wedellsborg. Zeit. phys. Chem.* **22**, *222* (*1897*). A theorem of Poynting is used to show that no damping of the electric vibrations of an absolute conductor need ever occur, which—assuming a luminous molecule to behave like a conductor with a vibrating charge—is made to illustrate Ostwald's conclusion that bodies probably lose no energy through radiation into empty space. *J. E. T.*

Electric Abnormality and Chemical Constitution. *P. Drude. Ber. sächs. Ges. Wiss.* **1896**, *431; Wied. Ann.* **60**, *500* (*1897*). In a previous paper, this Journal **1**, 454, the author has shown that rapid electric oscillations are much more readily absorbed by certain liquids than the conductivities of the latter for constant currents would lead one to expect. The present paper contains the results of measurements on twenty substances with a view to determine which of them exhibit this abnormal absorption for waves of 75 cm in length. Like the refractive index for light and for electric waves, the electric abnormality seems to be essentially a *constitutive* property: Water, the hydrocarbons, ethers, ketones, aldehydes, and the haloid derivatives of the paraffins, are normal; while alcohols, especially those with high molecular weights, acids, phenol and sugar (in solution) exhibit abnormality; all of the latter class contain the hydroxyl group. Acetacetic ether is normal, oxalacetic ether abnormal, this may be regarded as an argument in favor of the keto-formula for the former and the hydroxyl formula for the latter.

With the author's apparatus a measurement may be made inside of five minutes with 0.25 cc substance; and the value of the method is still further enhanced by the result of experiments with frozen phenol, formic and acetic acids, which go to show that the same regularities hold for solids as for liquids. *W. L. M.*

A New Physical Contribution to the Determination of Chemical Constitution. *P. Drude. Ber. chem. Ges. Berlin,* **30**, *940* (*1897*). Experiments on 140 substances, mostly organic, with the author's apparatus for detecting the absorption of electric waves. Water, ethyl-phenyl-ketone and monobromnaphthalene form the only exceptions to the rule that absorption (in liquids) is conditional on the presence of hydroxyl. In solutions also, when concentrated enough, the presence of hydroxyl may be detected by the absorption; the behavior of solids, however, is less reliable, as many substances which exhibit well marked absorption in the liquid state do not absorb at all when solid. In general the absorption is decreased by rise in temperature. The author applies his results in discussing the structures of tautomeric bodies and in cases where the constitution is still uncertain. A full description of the necessary apparatus is to be given in the Zeit. phys. Chem; it may be procured from Mechaniker Donner of the Leipzig physical institute. *W. L. M.*

The Refractive Indices of Certain Substances for very Short Electric Waves. *A. Lampa. Sitzungsber. Akad. Wiss. Wien.* **105**, *IIa, 587 (1896)*. The author describes a modification of Lebedew's method, by means of which waves of only six millimeters in length may be employed. The solid substances (paraffin, ebonite, crown and flint glass, sulfur, wood) were cut into prisms, the liquids (benzene, glycerol, turpentine, vaseline, benzaldehyde, alcohol, water) were examined in a hollow prism of ebonite and glass. Abnormal dispersion was noticed in the case of benzene, glycerol and alcohol; not in that of water. *W. L. M.*

Experiments on the Chemical Action of Electrical Oscillations, I. *A. de Hemptinne. Zeit. phys. Chem.* **22**, *358 (1897.)* When carbon disulfid is decomposed the products are solids and the author has succeeded in showing that this is a monomolecular reaction. The rate of decomposition of ammonia can not be represented by an equation of the fourth order and apparently no other was considered. The length of the discharge affects the rate of decomposition. With increasing pressure the equilibrium between ammonia and its decomposition products is displaced towards the ammonia side. *W. D. B.*

Determination of the Dielectric Constants of Some Salt Solutions by the Electrometric Method. *F. J. Smale. Wied. Ann.* **60**, *625 (1897.)* The measurements were made in 1895; but have been held back in hopes of confirming the results by an independent method. The author found that the dielectric constant of solutions of electrolytes rises with increasing concentration; but not proportionally to the change in conductivity. *W. D. B.*

On the Use of Rapid Electric Oscillations with the Wheatstone's Bridge. *W. Nernst. Wied. Ann.* **60**, *600 (1897)*. The author describes in detail a method for determining dielectric constants with the Wheatstone's bridge, using alternating currents of high frequency obtained by the oscillating discharge of a condenser. As indicator a spark gap or a vacuum tube was used, but the author discusses the possibility of using other instruments. *W. D. B.*

On the Viscosity of Salt Solutions and their Mixtures. *A. Kanitz. Zeit. phys. Chem.* **22**, *336* (*1897*). The author finds that the formula of Arrhenius applies very well to most mixed solutions. The exceptions are said to be due to polymerization of one sort or another. *W. D. B.*

The Viscosity of Mixtures of Miscible Liquids. *T. E. Thorpe and J. W. Rodger. Jour. Chem. Soc.* **71**, *360* (*1897*). From a study of carbon tetrachlorid and benzene, methyl iodid and carbon bisulfid, ether and chloroform, the authors conclude that «the viscosity of a mixture of miscible and chemically indifferent liquids is rarely, if ever, under all conditions, a linear function of the composition». The viscosity is usually lower than the mixture rule would indicate; but with ether and chloroform the contrary result is obtained at low temperatures. The paper thus confirms the facts previously noted by Wijkander and Linebarger. *W. D. B.*

An Experimental Investigation of the Equilibrium of the Forces acting in the Flotation of Discs and Rings of Metal. *A. M. Mayer. Am. Jour. Sci.* [*4*] **3**, *253* (*1897*). After giving formulas connecting the surface tension of a liquid surface with the forces of gravity and pressure at the instant when a ring or disc sinks by breaking through the surface the author describes a number of experiments. The metals were very carefully cleaned and fresh distilled water surfaces were used. Experiments on three aluminum discs gave $T = 0.0767$, 0.0821 and 0.0787 [gm.cm^{-1}]. For wire rings of diameters from 5.46 cm to 5.18 cm, the thickness of the wire being 1 mm, the values found for T_{16° were iron 0.0802, tin 0.0810, copper 0.0813, brass 0.0810 and German silver 0.0811. The mean is 0.0809. The mean of twenty-eight determinations made during the last sixty years by various observers is 0.0772 when all are reduced to 0° by Brunner's formula. For a NaCl solution in water (sp gr $= 1.2$) $T_{16^\circ} = 0.0860$ assuming the true value for water to be 0.0772. If the rings are heated in a spirit flame they will not float until they have remained some minutes in the air. Apparently a surface layer of air is needed to prevent the water from wetting the metal. For numerous experimental details we must refer the reader to the original. *E. B.*

On the Influence of the Temperature on the Surface Tension Water and Other Liquids. II. *V. Monti. Nuovo Cimento,* (4) **5**, *186* (*1897*). The author's experiments lead him to reject Jäger's hypothesis that the change in the temperature coefficient of the surface tension in passing from a pure liquid to a solution is independent of the nature of the solute. He finds that Sutherland's formula for the surface tensions of mixtures of «normal» liquids applies also to paraffin in ether or carbon bisulfid and to sulfur in carbon bisulfid. *W. D. B.*

Are Diphenyliodonium and Thallium Nitrates Isomorphous? *Noyes and Hapgood. Zeit. phys. Chem.* **22**, *464*. Reviewed in this Journal **1**, 249, from other sources.

The Crystalline Form of Optically Active Substances. *H. Traube. Ber. chem. Ges. Berlin,* **30**, *288* (*1897*). The author upholds his statement that «in all cases where a *complete* determination of crystalline symmetry has been carried out, Pasteur's generalization as to the form of optically active substances has been confirmed.» He charges Walden with a want of comprehension of modern crystallography and invites him to continue the discussion in a crystallographic journal. *W. L. M.*

On the Structure of Metals, its Origin and Changes. *F. Osmond and W. C. Roberts-Austen. Phil. Trans.* **187** (A), *417* (*1897*). An abstract of this paper has already appeared, Proc. Roy. Soc. **60**, 148 (1896) and was reviewed in this Journal **1**, 336 (1897.)

On the Volatility of Compounds containing Fluorin. *L. Henry. Bull. Acad. roy. Belg.* (*3*) **33**, *195* (*1897*). The substitution of fluorin for hydrogen in a hydrocarbon produces little change in the boiling point. If the compound already contains a halogen, the substitution of hydrogen by fluorin lowers the boiling point. This is in accord with the author's rule that increasing the number of negative radicals increases the volatility. *W. D. B.*

ON THE SECOND DIFFERENTIAL COEFFICIENTS OF GIBBS' FUNCTION ζ. THE VAPOUR TENSIONS, FREEZING AND BOILING POINTS OF TERNARY MIXTURES

BY W. LASH MILLER

The Second Differential Coefficients of ζ

In his paper on «Equilibrium in Heterogeneous Systems» Professor Gibbs[1] introduces a function

$$\zeta = \varepsilon - t\eta + pv \qquad (91)$$

and shews that

$$d\zeta = -\eta dt + vdp + \mu_1 dm_1 + \mu_2 dm_2 + \ldots + \mu_n dm_n \qquad (92)$$

As will be seen from its definition in (91), ζ is a quantity whose value for any given system depends only on the values of the physical parameters π describing the state of that system for the time

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[1] *Trans. Conn. Acad. III (1876–1878).*

The letters have the same meaning as in the work of Gibbs referred to, ε energy, t absolute temperature, p pressure, v volume, η entropy, m_1 mass and μ_1 potential of the substance indicated by the suffix. μ_1 is defined by the equation $\mu_1 = (\partial\varepsilon / \partial m_1)_{\eta, v, m}$. The small letters to the right of the differential coefficients (*e. g.* η, v, m in the last equation) indicate the quantities remaining constant during the differentiation ; m (short for $m_2, m_3 \ldots m_n$) indicates all the quantities $m_1 \ldots m_n$ except that one (m_1) mentioned in the differential coefficient.

The expressions for the potential μ of a gas in Gibbs' work are deduced with the aid of the equation $pv = at$. In the present paper this equation has been replaced by the more convenient $pv = nRt$. Consequently in numerical applications of the equations in the text, the quantities of the various components must be expressed in «gramme molecules» not in grammes. This has been indicated by replacing the letters m_1, m_2, etc., by $n_1, n_2 \ldots$ wherever necessary. The numbers of the equations, *e. g.* (91) above, refer to Gibbs' paper *l. c.*

being, and is independent of the manner in which that state has been attained. The values of the second differential coefficients of ζ must consequently be independent of the order of differentiation, or

$$\frac{d^2\zeta}{d\pi_1, d\pi_2}{}_{\pi} = \frac{d^2\zeta}{d\pi_2, d\pi_1}{}_{\pi} \qquad \text{A}$$

From equation (92) there follows:

$$\frac{d\zeta}{dt}{}_{p,m} = -\eta \qquad \frac{d\zeta}{dp}{}_{t,m} = v \qquad \frac{d\zeta}{dm_1}{}_{t,\,p,\,m} = \mu_1 \quad \textit{etc., etc.}$$

Substituting these values in A there results a set of equations of the form

$$\frac{d\eta}{dp}{}_{t,m} = -\frac{dv}{dt}{}_{p,\,m} \qquad -\frac{d\eta}{dm_1}{}_{t,\,p\,m} = \frac{d\mu_1}{dt}{}_{m,\,p.}$$

$$\frac{dv}{dm_1}{}_{t,\,p,\,m} = \frac{d\mu_1}{dp}{}_{t,\,m} \qquad \frac{d\mu_1}{dm_2}{}_{t,\,p,\,m} = \frac{d\mu_2}{dm_1}{}_{t,\,p,\,m}$$

One of these, that connecting dv and $d\mu_1$, has been made use of by Gibbs[1]. The object of the present paper is to illustrate the importance, for the theory of ternary mixtures, of the last on the list, viz:—

$$\frac{d\mu_1}{dm_2}{}_{t,\,p,\,m} = \frac{d\mu_2}{dm_1}{}_{t,\,p,\,m} \quad \textit{etc.} \qquad \text{B}$$

NOTE. Although in equation B, p is represented as a constant, if the potentials μ_1 μ_2 refer to components of a liquid or solid mixture they will not be affected by moderate[1] variations in p.

The Interpretation of μ in Equation B

An idea of the great number of special applications that may be made of equation B can best be gained from a review of the different methods by which the potentials μ may be measured. Gibbs has shewn how *μ for a gas*[2], and μ_1, μ_2 . . . for the components of a gaseous mixture[3], may be expressed as functions of the various physical coördinates which may be employed to describe the thermodynamical state of a gas. For a *liquid or solid phase* he has shewn the connection between the potentials of the various components and

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[1] Gibbs. l.c. equation 272, page 214.

[2] Gibbs. l.c. equations 259, 264, 268, pages 211 and 212.

[3] Gibbs. l.c. page 215.

their *vapour tensions*[1] (partial pressures). The relation between the vapour tension (consequently μ) and the *freezing point* of a solution was worked out by Guldberg[2]; while Arrhenius employed the well known formula of Clausius to connect the vapour tension of a solution with its *boiling point*[3]. An ingenious speculation ‹on the value of the potentials when the quantity of one component is very small›[4] led Gibbs to the assumption of a relation between the potential and the *concentration* of a substance in dilute solution, which was afterwards shewn to hold for all substances whose vapours dissolve according to *Henry's law*[5]. From a paper by van 't Hoff may be deduced the corresponding relation for vapours which dissolve according to a modified (‹*potentized*›) *Henry's law*[6], while Nernst's theory of distributive equilibrium[7] opens up the case where the vapour phase is replaced by a *second liquid*.

Osmotic Pressure. ($\mathfrak{P}$) was brought into connection with vapour tension (and hence with μ) by van 't Hoff[8]; and the experimental confirmation of his equation $\mathfrak{P}\mathfrak{V} = nRt$, shews that the relation discerned by Gibbs holds for many substances which have never been gasified. Arrhenius lastly shewed how abnormal ‹molecular weights in solution› (on which the values of n in van 't Hoff's equation depend) may in many instances be predicted from measurements of the *electrical conductivity*[9] of the solution; as a result of the development of the Arrhenius–van 't Hoff theory, it is now possible in many cases to express the potential μ of a dissolved substance as a function of its concentration in the solution, without any knowledge of its behaviour in the form of gas. The *electromotive force* of certain cells was connected with the potentials of the reacting sub-

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[1] Gibbs. l.c. page 225.

[2] Guldberg. C.r. **70**, 1349.

[3] Arrhenius. Zeit. phys. Chem. **4**, 550 (1889).

[4] Gibbs. l.c. equation 216, page 196.

[5] Gibbs. l.c. page 226.

[6] Van 't Hoff. K. Svenska Vet. Akad. Handl. **21**, 21 (1887).

[7] Nernst. Theoretische Chemie.

[8] van 't Hoff. Études de dynamique chimique, p. 182 (1884).

[9] Arrhenius. Zeit. phys. Chem, **1**, 631 (1887).

stances by Gibbs[1] in the work referred to; and Nernst[2] by connecting E.M.F. with osmotic pressure has done much to make this relation better understood.

The object of this paragraph is to shew what a very large number of important relations may be deduced from equation A, by replacing the terms μ_1, μ_2, *etc.*, by their values in terms of the physical quantities enumerated. In the present paper only those applications will be considered in which the potential of one at least of the substances involved is expressed as a function of its *solubility* in the mixture under consideration.

μ *as a function of solubility*

In a solution saturated with a solid, S, the potential μ_S of a given weight ($n_{,}$ gramme molecules) of the substance S is equal to that of the same weight of the solid at the same temperature (and pressure). The potential $\mu_{,}$ of the same weight of the same substance in a more dilute solution is less than μ_S and assuming

$$\mathfrak{P}\mathfrak{V} = n_{,}Rt$$

there follows

$$\mu_{,} = \mu_S + n_{,}Rt \log \text{nat}\ \mathfrak{P}_{,}/\mathfrak{P}_S \qquad (t\ \text{const.})$$

in which $\mathfrak{P}_{,}$ is the osmotic pressure of the salt in the dilute solution and $\mathfrak{P}_S$ that in the saturated solution.

By differentiation,

$$d\mu_{,} = nRtd \log \text{nat}\ \frac{\mathfrak{P}_{,}}{\mathfrak{P}_S}$$

or, if $\mathfrak{P}_{,}/\mathfrak{P}_S$ be set equal to $C_{,}/C_S$ (the ratio of the concentrations[3] of S in the two solutions)

$$d\mu_{,} = n_{,}Rt\,d \log \text{nat}\ C_{,}/C_S \qquad \text{C.}$$

If then solutions of the substance S be prepared of equal concentrations in different solvents, the potential $\mu_{,}$ will be greatest for that solution which is nearest saturated; or the greater the solubility of

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[1] Gibbs. l.c. page 501.

[2] Nernst. Zeit. phys. Chem. 4, 129 (1889).

[3] This is allowable only when the molecular weight of S is approximately the same in the two solutions.

S in any solvent the less the potential μ_s for any given concentration. If to a solution of S in a liquid mixture of A and B there be added an additional quantity of A, the potential μ_s will be *increased* if less S can dissolve in the mixture after addition of A than before, and *vice versa*. It is not sufficient that S should be less soluble in A than in B, or in mixtures containing a large percentage of A than in those with a less; *the total quantity of S that can dissolve must be lessened by addition of A to the solvent.* This is one of the most important (qualitative) conclusions from equation C.

Solubility and Electromotive Force

The relation expressed in equation C may be made use of in calculating the E.M.F. of cells of the type

metal M / salt MX in water / salt MX in dil. alcohol / metal M.

If the aqueous and alcoholic solutions of MX be of the same concentration, the current will pass within the cell from the water to the cell alcohol (assuming MX less soluble in alcohol than in water) and the electromotive force will be

$$E.M.F. = \frac{v}{u+v}\frac{n_t}{n_e}\, 0.0002\, t \log \frac{C_W}{C_A}$$

where C_W and C_A are the concentrations of saturated solutions of MX in water and in the dilute alcohol respectively. (The substitution of C for $\mathfrak{C}$ is allowable only when the molecular weight of MX is the same in both solutions, and where MX is not very soluble in either).

The Freezing Points of Ternary Mixtures

The subject has been treated of in the May number of this Journal by Mr. D. McIntosh[1]. He finds:—

"When we have two non-miscible substances A and C and a third substance B with which the other two are miscible[2], we can distinguish two cases.

(i) The component A can exist as solid phase under the conditions of the experiment. Under these circumstances addition of C to the liquid phase containing A and B will raise the temperature at

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[1] D. McIntosh. Solubility and Freezing Point. This Journal 1, 474 (1897).

[2] NOTE. The letters A, B and C will be used in this sense throughout the remainder of this paper.

which A can exist as solid phase [illustrated by experiments with benzene (A), alcohol (B) and water (C)].

(ii) The component B can exist as solid phase under the conditions of the experiment. Under these circumstances addition of C to the liquid phase will lower the temperature at which B can exist as solid phase [illustrated by the experiments of Abegg[1] and others on the freezing points of solutions of salts in aqueous alcohol, *etc.*]»

The connection between these propositions and the requirements of equation B may be seen from the following considerations. As the substance C is soluble in B but not in A, it is fair to assume that its solubility in mixtures of A and B will decrease with rise in the proportion of A in the mixture. If the decrease in solubility should be so rapid that (as is the case with the mixtures of benzene, alcohol and water) addition of A precipitates C from its saturated solution in a mixture of A and B, then, by equation C

$$\frac{d\mu_c}{dm_c}{}_{t,p,m} \text{ is positive}$$

and consequently (by equation B)

$$\frac{d\mu_a}{dm_c}{}_{t,p,m} \text{ is positive}$$

or, on addition of C the potential of A, and consequently its vapour tension and the temperature at which it is in equilibrium with solid A, will rise. McIntosh's second case, as quoted above, is the converse of the first.

In order to throw further light on this *second case* it is convenient to introduce another of Gibbs' equations.

$$0 = -v\,dp + \eta\,dt + m_1 d\mu_1 + m_2 d\mu_2 + \ldots + m_n d\mu_n \qquad \text{(97[2])}$$

which for liquid mixtures of three components, kept at constant temperature and fairly constant pressure, becomes

$$0 = m_a d\mu_a + m_b d\mu_b + m_c d\mu_c \qquad \text{D}$$

It has just been shewn that addition of C, which involves an increase

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[1] Abegg. Zeit. phys. Chem. 15, 260 (1894).

[2] Gibbs. l.c. page 143.

in μ_c (see equation C), increases the value of μ_a as well. To satisfy equation (97) the value of μ_b must diminish, and it will readily be seen that the less soluble C is in A (consequently the greater the change in μ_a on addition of C), the greater will be the diminution in the value of μ_b. The experimental evidence on this point has been collected by McIntosh who finds that:—

«Addition of C will lower the temperature at which B can exist as solid phase, and this lowering will be more than it would be if A and C were miscible to some extent».

«The freezing point is lowered if the substance added be non-miscible with the component which does not appear as solid phase, and this lowering is greater than if the substances were added to the pure solvent».

The considerations advanced in this paragraph and in that on ‹μ as a function of solubility› may serve further to connect the two apparently isolated facts (*i*) that the solubility of a mixture of two solids in a common solvent is usually not the sum of their individual solubilities, and (*ii*) that the depression in the freezing point of a solvent produced by dissolving in it a mixture of two substances is in general not equal to the sum of the separate depressions, even when the dissolved substances seem incapable of acting chemically on each other.

The Vapour Tensions of Ternary Mixtures

If μ_a be expressed in terms of p_a (the partial pressure of A in the vapour given off by the mixture), and μ_c as in equation C, equation B takes the form

$$n_a \frac{d \log \text{nat}\, p_a}{dn_c}{}_{t,p,n} = n_c \frac{d}{dn_a} \log \text{nat} \frac{C_c}{C_{\mathcal{C}}}{}_{t,p,m} \qquad \text{E}$$

Similarly with p_c, *etc.*

More or less empirical formulae to represent the alterations in the composition of the vapour (distillate) on addition of C may be deduced by combining equation E with the expressions found by Bodländer[1] and by Bancroft[2] and his pupils for the solubility of salts

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[1] Bodländer. Zeit. phys. Chem. 7, 308 (1891).

[2] Bancroft. This Journal 1, 34 (1896).

in aqueous alcohol, *etc.* On the other hand, from measurements of the partial pressures of the vapours given off by mixtures of A and B, and of the alterations in them produced by addition of C, the molecular weight of the latter in the solution (hence n_c in equation E) may be determined[1]; and then, by means of equation E, the form of the solubility isotherms for C in mixtures of A and B.

The Boiling Points of Ternary Mixtures

If only *one* of the components be sensibly volatile at the temperatures of the experiment, the problem is very simple. If A be volatile, addition of C will increase the vapour tension or lower the boiling point of the mixture. If B be volatile the reverse is true.

If on the other hand both A and B have a noticeable vapour tension, while C has not, (for example alcohol (A), water (B), salt (C)), the change in the total vapour tension of the mixture on adding C is the algebraical sum of the changes in the partial pressures of A and B. In the case selected for illustration, addition of salt increases the vapour tension of the alcohol and diminishes that of the water. Whether the *total* tension will be increased or the reverse (*i. e.* whether the boiling point of the mixture will be lowered or raised by addition of C) depends on two circumstances.

(i) *The form of the curve of solubility of C in mixtures of A and B.* If alterations in the proportions of A and B in the mixture has but little effect on the solubility of C, the addition of C will bring about little or no increase, or even a diminution in the vapour tension of A; it is only when the quantity of C that can dissolve in a given mixture of A and B is lessened by addition of A that the vapour tension of A will be increased by addition of C. When C is equally soluble in all mixtures of A and B, the composition of the vapour will be unaffected by addition of C; cases of this nature were selected by Nernst and Roloff[2] for the determination of molecular weights in mixed solvents by means of the ebullioscope.

(ii) *The relation between the proportion of A to B in the Solution and in the vapour given off by it.* This may be illustrated by

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[1] By means of Gibbs' equation (97). See also Nernst, Zeit. phys. Chem. **11**, 1, (1893.)

[2] Roloff. Zeit. phys. Chem. **11**, 7 (1893).

the case of mixtures of propyl alcohol (A), water (B), and salt (C)—the vapour given off by 75 percent propyl alcohol has the same composition as the boiling liquid, while if the liquid contain more alcohol the vapour contains less and *vice versa*.

By substituting for μ_a and μ_b their values in terms of the vapour tensions p_a and p_b of the alcohol and the water in the mixture, equation D becomes

$$-n_b Rtd\log \text{nat} \, p_b = n_a Rtd\log \text{nat} \, p_a + m_c d\mu_c$$

whence

$$-\frac{\partial p_b}{\partial p_a} = \frac{p_b}{p_a} \cdot \frac{n_a}{n_b} \qquad \text{F}$$

and for 75 percent alcohol, (where $p_b : p_a = n_b : n_a$)

$$-\partial p_b = \partial p_a$$

From this it follows that the total diminution in the vapour tension of 75 percent propyl alcohol on addition of salt, will be numerically equal to the diminution that would have been produced in the tension of the water vapour alone if the tension of the alcohol had not been affected by the addition of the salt. The conditions under which the boiling point of a mixture of alcohol and water is unaffected by addition of salt, may be obtained by combining equations C and F and introducing the condition

$$dp_a + dp_b = o$$

My attention was first attracted to the subject of this paper by a measurement made in this laboratory in 1893 by Mr. F. B. Kenrick, who observed that the boiling point of aqueous alcohol was lowered by the addition of potassium chlorid, and found that, as suspected, the percentage of alcohol in the distillate was increased by the addition of the salt. Measurements made last autumn together with Mr. T. R. Rosebrugh, by means of an apparatus similar to that employed by Lehfeldt[1] gave the following results:

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[1] Phil Mag. 1895.

Solution *i.* consisted of 46.27 percent alcohol.
Its vapour tension at 54°.6 — 54°.9 C was 232 *mm.* Hg.
The vapour consisted of 82.18 percent alcohol.
Solution *ii.* consisted of 330.4 grammes of 46.27 percent alcohol in which were dissolved 28.1756 grammes of sodium chlorid.
Its vapour tension at 54°.7 C was 244 *mm.* Hg.
The vapour consisted of 85.85 percent alcohol.

From these data there follows :

Solution *i.* Tension of the alcohol 190.6 *mm*, of the water 41.4 mm.
Solution *ii.* " " " 209.5 " " " 34.5 "

Difference + 18.9 mm — 6.9 mm.

The boiling point of solution *ii* determined in a Beckmann's apparatus was 0.9° C lower than that of solution *i.* (Bar. 759 *mm.* B.pt. about 82° C).

Owing to the great influence which slight errors in determining the composition of the vapour exert on the value obtained for the molelcular weight of the salt, the work was laid aside until a more accurate means of arriving at the composition of the vapour could be devised. At present, Mr. Rosebrugh and myself are engaged with a much improved apparatus, in determining the partial pressures of the vapours given off at different temperatures by aqueous alcohol of different strengths; we hope also to obtain material with which to test the relations discussed above.

The Chemical Laboratory of the University of Toronto,
May, 1897.

SOME BOILING-POINT DETERMINATIONS

BY H. J. STEUBER

Quite recently there appeared a paper by Freyer[1] on the boiling-points of solutions containing alcohol, sugar and water. He found that when the amounts of the two solutes were expressed in volume concentrations, the presence of sugar lowered the boiling-point instead of raising it. If, however, the concentrations of the alcohol and sugar are given in grams per liter, the concentration of the water necessarily changes with changing amounts of sugar. Of more importance is the fact that the ratio of alcohol to water increases with increasing concentration of sugar and the lowering of the boiling-point might be due chiefly to that. In order to settle the question I have made several measurements with the Orndorff apparatus, adding alcohol and then sugar to a constant quantity of water. In all cases the boiling-point rose on adding sugar. The experiments were then repeated, substituting sodium chlorid for sugar. The result was the same as in the preceding case.

It seemed desirable to determine the effect, if any, of the presence of alcohol on the change of boiling-point due to the addition of salt. Since salt and alcohol are not miscible to any appreciable extent, one effect of adding salt must be to increase the partial pressure of the alcohol vapor and therefore to diminish the rise of boiling-point and to increase the apparent reacting weight. On the other hand it has already been shown[2] that the decrease in the partial pressure of the solvent due to the presence of two solutes is greater than the sum of the changes due to each solute when the solutes are non-miscible. The effect of this would be to increase the

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[1] Zeit. angew. Chem. **1896**, 654.

[2] McIntosh, Jour. Phys. Chem. **1**, 474 (1897).

boiling-point and to diminish the apparent reacting weight of the sodium chlorid. At present there is no way of predicting which of these effects will be the greater and it seems not impossible that in some cases the one might predominate and in others the other.

My measurements with sodium chlorid are given in Tables I–II. Opposite the word alcohol is given the amount of this substance in one kilogram of water and the lowering of the boiling-point actually observed. The values K and M are calculated from the formula $\frac{g}{\Delta}K = M$, taking $M = 58.5$ when calculating K and $K = 0.520$ when calculating M. Under g is the amount of sugar in grams per kilogram of water and under Δ is given the rise of boiling-point measured from the boiling point of the alcohol-water mixture as zero.

TABLE I

Barometer. 745.3 mm

Alcohol 8.37 g = — 0.450°

g	g/M	Δ	K	M
2.79	0.048	0.040°	0.838	36.3
5.36	0.092	0.060	0.655	46.5
10.21	0.175	0.130	0.745	40.8
14.38	0.246	0.190	0.773	39.4
21.74	0.372	0.300	0.807	37.7
30.56	0.522	0.450	0.861	35.3
43.02	0.736	0.640	0.869	35.0
54.45	0.925	0.840	0.908	33.5

In the first series there was very little alcohol and the effect would therefore be correspondingly small. If we omit the first determination, in which the percentage error is very large, we see that the apparent reacting weight of sodium chlorid decreases regularly from about forty-six to thirty-three. If sodium chlorid were completely dissociated, and there were no disturbing factors we should get an apparent reacting weight of a little over twenty-nine and a value K = 1.04. It is clear that, in this particular case, the

TABLE II

Barometer. 741.5 mm

Alcohol 18.53 g = — 1.585°

g	*g*/M	Δ	K	M
8.54	0.146	0.065°	0.446	68.2
19.69	0.337	0.155	0.45	66.1
33.68	0.575	0.295	0.513	59.3
42.30	0.723	0.425	0.587	51.8
59.41	1.016	0.595	0.586	51.9
73.77	1.262	0.765	0.607	50.1
88.69	1.486	0.935	0.630	48.3
106.65	1.824	1.145	0.628	48.4
123.39	2.006	1.365	0.647	47.0

presence of alcohol increases the apparent reacting weight and that this effect diminishes as the ratio of salt to alcohol increases. In the second series the effect of the alcohol is much more marked, the apparent reacting weight of the sodium chlorid being higher in the first three measurements than it would be if sodium chlorid were a non-electrolyte and no alcohol were present. This disposes of the criticism which might have been urged against the first series, that the increase in the apparent reacting weight was due to a decrease in dissociation caused by the addition of alcohol.

One set of measurements was made with sugar and eighty per-cent alcohol. The first addition of sugar produced an apparent lowering of the boiling-point but the change is so small, 0.005°, that no stress is to be laid upon it. Further addition of sugar caused a rise of the boiling-point. This rise is so small that if the alcohol were ignored and only the ratio of sugar to water were taken into account we should find an apparent reacting weight of five to six thousand for sugar. This of course means nothing and is merely a striking instance of the precipitation of alcohol by sugar. The data are given in Table III. Under g_1 are grams of sugar in one kilogram of aqueous alcohol; under *g* are grams of sugar in one kilogram of water and under Δ the changes of boiling-point, a rise being considered positive.

TABLE III

Barometer. 743.0 mm

g_1	g	Δ	g_1	g	Δ
15.8	63.2	−0.005°	97.8	391.2	0.030°
29.6	118.4	+0.000	113.9	455.6	0.040
44.3	177.2	0.010	127.6	510.4	0.050
57.9	231.6	0.020	138.7	554.8	0.060
68.6	274.4	0.025	152.6	610.4	0.060
82.1	328.4	0.030			

Cornell University; May, 1897.

TWO LIQUID PHASES

SECOND PAPER

BY WILDER D. BANCROFT

In the preceding paper[1] I discussed the temperature changes along the boundary curve for solid phase, two solutions and vapor. It was shown that a knowledge of the solubility relations among the components is essential to a clear understanding of the facts. In this paper it is my intention to show the general forms of the projected concentration-temperature diagram for three-component systems in which two solution phases are possible[2]. In considering the complete diagram it will be advisable to adopt a classification differing somewhat from that used in the preceding paper where the only question was the change of freezing-point on addition of the third component. The main divisions of the subject are into systems in which one pair of components can form two liquid phases, in which two pairs of components can form two liquid phases and in which three pairs can be treated as partially miscible liquids. The relative miscibilities can then be taken as a basis for a farther subdivision. We will postulate that we start in all cases with three substances, A, B and C, which form no compounds ; that the melting point of A is higher than that of B and that A and B can form the binary nonvariant system, solid A, two solutions and vapor. The following are then natural divisions of the subject :

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[1] Jour. Phys. Chem. **1**, 414 (1897).

[2] Schreinemakers is treating the same subject from a different point of view, Zeit. phys, Chem. **22**, 93, 515 (1897). He takes the thermodynamic potential as one of the coordinates instead of the temperature.

- I. A and C, B and C do not form two liquid phases.
  - 1. C increases the miscibility of A and B.
    - a. Quintuple point with A and C as solid phases.
    - b. Quintuple point with A and B as solid phases.
    - c. No quintuple point with two liquid phases.
  - 2. C dissolves in A with precipitation of B.
    - a. Quintuple point with A and C as solid phases.
    - b. Quintuple point with A and B as solid phases.
    - c. Quintuple points with A and B, B and C as solid phases.
  - 3. C dissolves in B with precipitation of A.
    - a. Quintuple point with A and C as solid phases.
- II. B and C can form two liquid phases while A and C can not.
  - 4. C dissolves in A with precipitation of B.
    - a. Quintuple point with A and C as solid phases.
    - b. Quintuple point with A and B as solid phases.
    - c. Quintuple points with A and B, B and C as solid phases.
- III. A and C can form two liquid phases while B and C can not.
  - 5. C dissolves in B with precipitation of A.
    - a. No quintuple point with two liquid phases.
- IV. Both B and C and A and C can form two liquid phases.
  - 6. a. Three liquid phases can not exist simultaneously.
    - b. Three liquid phases can exist simultaneously.

In all the diagrams the boundary curves, along which two liquid phases are in equilibrium are represented by dotted lines so as to call attention to them. The temperature changes are shown by the arrow heads which point in the direction of rising temperature.

According to our program we have first to consider the cases in which only one pair of components, A and B, can be treated as partially miscible liquids and under this main heading we begin with the instances in which addition of the third component C increases the miscibility of the other two. Fig. 1 is the diagram for 1a. Along E_1F_1 and E_2F_2 we have the monovariant system, solid A, two solutions and vapor, the temperature falling as we pass away from the side of the triangle. At F_1 and F_2 we have C appearing as solid phase and a quintuple point with A and C as solid phases. From a graphical point of view there is a distinct difference between such a quintuple point and one at which three solid phases coexist with one solution and vapor. There are always five boundary curves meeting in a quintuple point; but ordinarily we represent only three of these in a triangular diagram, omitting the one along which there is no vapor phase for purposes of convenience and the one along which there is no solution phase from necessity. When there are two liquid phases coexisting at a quintuple point, one or the other or both of the solutions must exist along every one of the five boundary curves and we therefore represent four of the five graphically, omitting only the one along which there is no vapor phase. To distinguish the two solutions we will call S_1 the solution represented by E_1F_1L and S_2 the solution represented E_2F_2L. Along E_1F_1 and E_2F_2 we have A, S_1, S_2 and vapor, as has already been

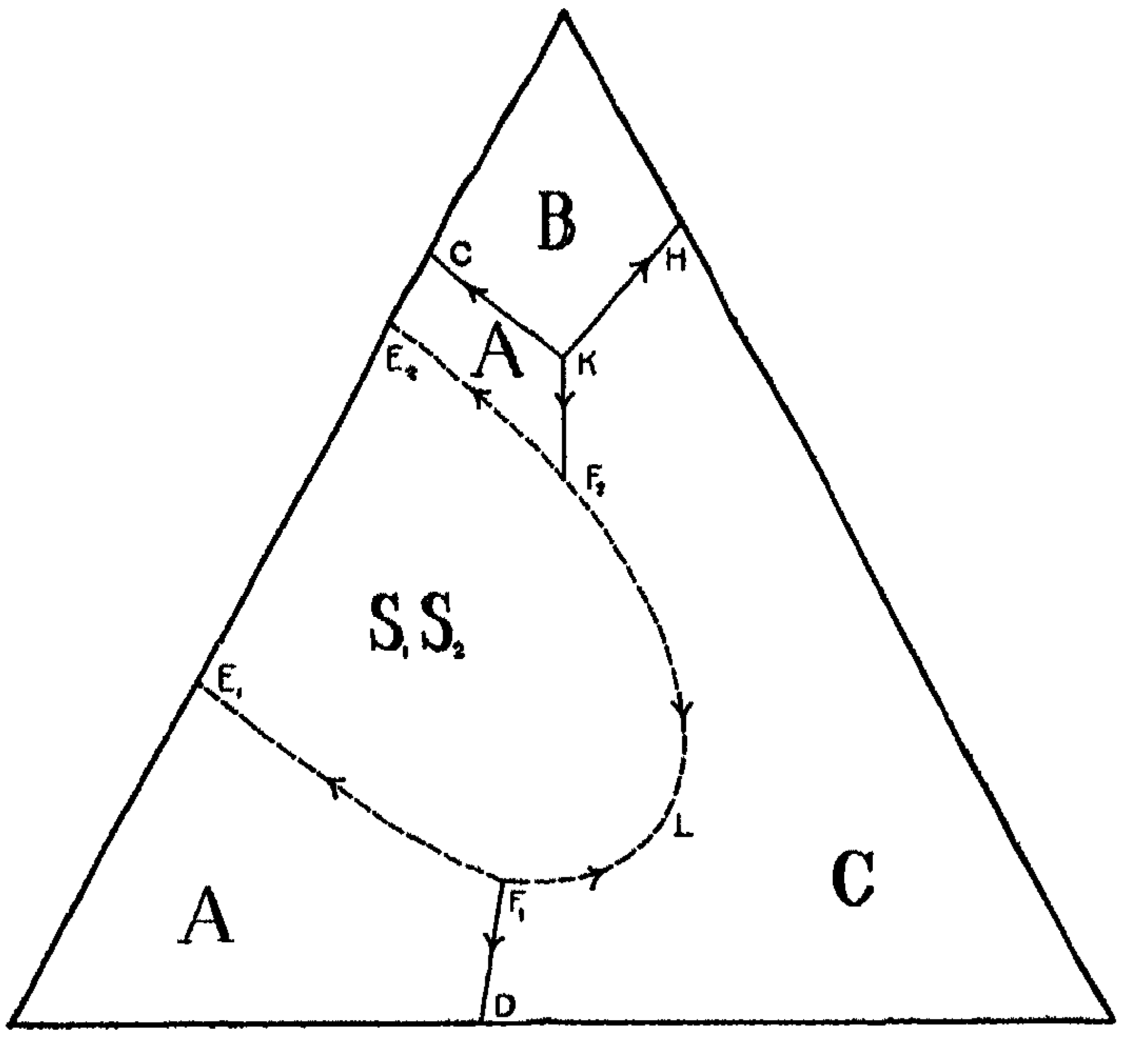

FIG. 1

pointed out. Along F_1L and F_2L we have C, S_1, S_2 and vapor in equilibrium. Along F_1D the phases in equilibrium are A, C, S_1 and vapor while A, C, S_2 and vapor exist along F_2K. The temperature rises as we pass from F_1 and F_2 to L, the point at which the two solutions become identical. The temperature rises in the direction F_1D according to the theorem of van Rijn van Alkemade.

If we start from the quintuple point represented by F_1 and F_2 and withdraw heat from the system, the temperature will remain constant until the whole of the first solution phase, S_1, has disappeared. The temperature will then fall and the system will pass along the curve F_2K until at K we have B appearing as solid phase and formation of the quintuple point with A, B, C, solution and vapor as the phases. This being a «primary»[1] quintuple point only three boundary curves are represented. Along F_2K we have A, C, solution and vapor; along KG, A, B, solution and vapor while B, C, solution and vapor are in stable equilibrium along KH. The temperature rises from the point K in all directions.

The divariant systems exist in the fields and we have A in equilibrium with solution and vapor in the part cut off by DF_1E_1 and also in the field E_2F_2KG, the solutions being different in the two cases. The component B occurs as solid phase in equilibrium with solution and vapor in the field cut off by GHK while the field for C is limited by HKF_2LF_1D. Two solutions and vapor occur in the space enclosed by the dotted lines $E_1F_1LF_2E_2$. I have never tried melting naphthalene and salicylic acid together; but if they are miscible in all proportions in the fused state, a diagram similar to Fig. 1 could probably be realized by letting A = naphthalene, B = water and C = salicylic acid.

If the difference between the melting points of A and B is not very great and if C is rather more soluble in A than in B, it may readily happen that we shall have a system corresponding to 1b in our classification. The diagram for such a system is given in Fig. 2. This differs so little from the preceding case that it need not detain us long. At F_1 and F_2 we have a «secondary» quintuple point with

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[1] So called to distinguish it from the «secondary» quintuple point F_1 and F_2 where there are two liquid phases.

A, B, two solutions and vapor as the five phases; at K there is a «primary» quintuple point with A, B and C as solid phases. The monovariant systems are A, S_1S_2 and vapor along E_1F_1 and E_2F_2; B, S, S_2 and vapor along F_1L and F_2L; A, B, S_2 and vapor along F_2G; A, B, S_1 and vapor along F_1K; A, C, solution and vapor along KD and B, C, solution and vapor along KH. The temperature rises to the sides of the triangle, to L and along KF_1. The fields for A are limited by E_1F_1KD and by E_2F_2G; the field for B lies to the right of and above GF_2LF_1KH; that for C is bounded by HKD while two solutions and vapor are to be found within the space shut off by $E_1F_1LF_2E_2$. This system could probably be realized with phenol as A, water as B and salicylic acid as C though here again this prediction must be taken as provisional since I know of no experiments on the behavior of salicylic acid in presence of phenol. It is possible also that benzene might be substituted for phenol.

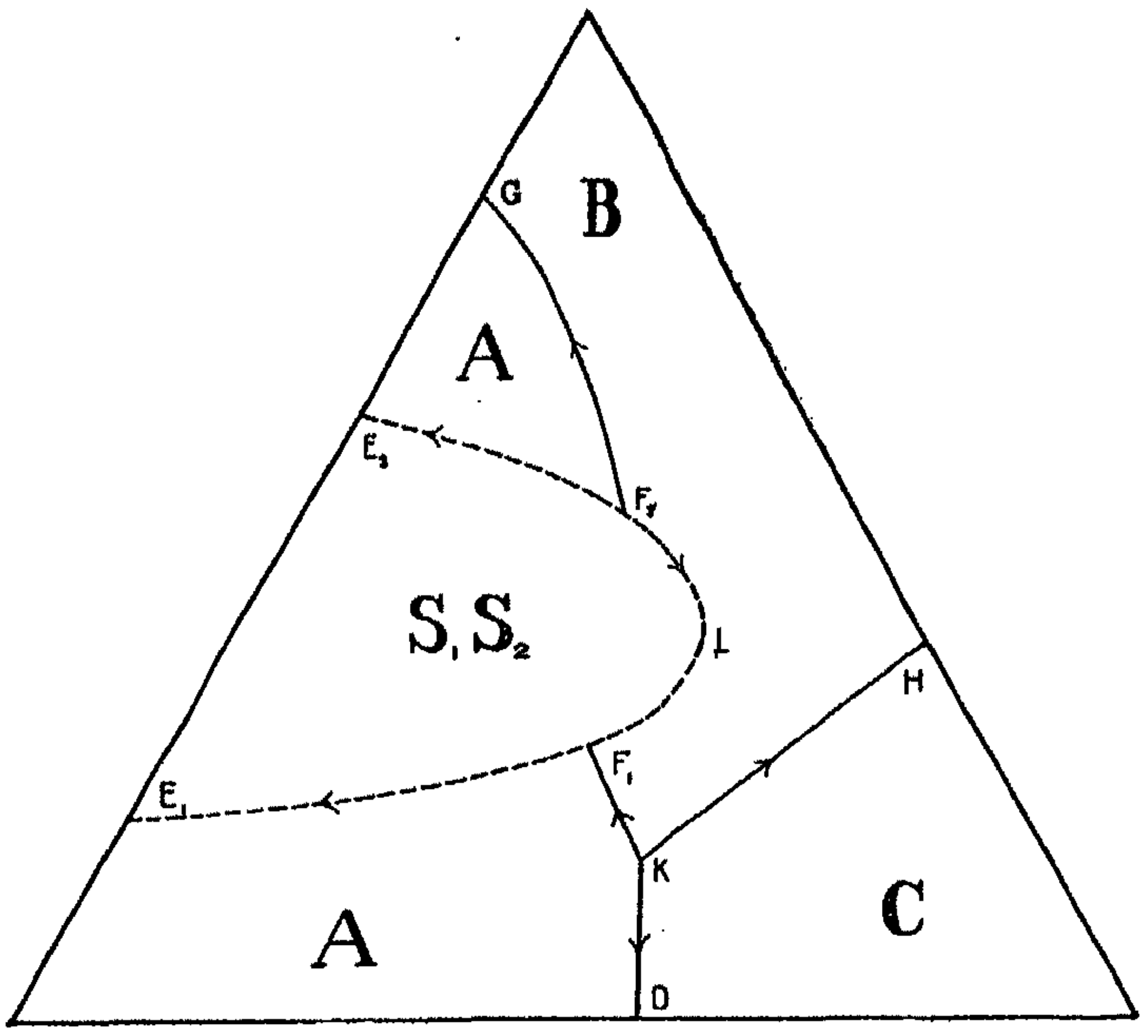

FIG. 2

If the melting points of both B and C be far below that of A it will often happen that the two solutions become identical before a new solid phase appears and there will therefore be no quintuple point with two liquid phases. The graphical representation of this type of equilibrium, 1c, is given in Fig. 3.

There is but one quintuple point, a «primary» one at K with A, B and C as solid phases. The boundary curves represented as radiating from this point are KD, KH and KG along which we have solution and vapor in equilibrium with A and C, B and C, A and B respectively. In addition there is a detached monovariant system represented by E_1L and E_2L. Along this curve the phases in equilibrium are A, two solutions and vapor. The temperature rises along each boundary curve in the direction of the side of the triangle. The divariant system, A, solution and vapor, exists in the area between E_1LE_2 and DKG; B is solid phase above GKH and C to the right of HKD while two solutions and vapor occur in the space

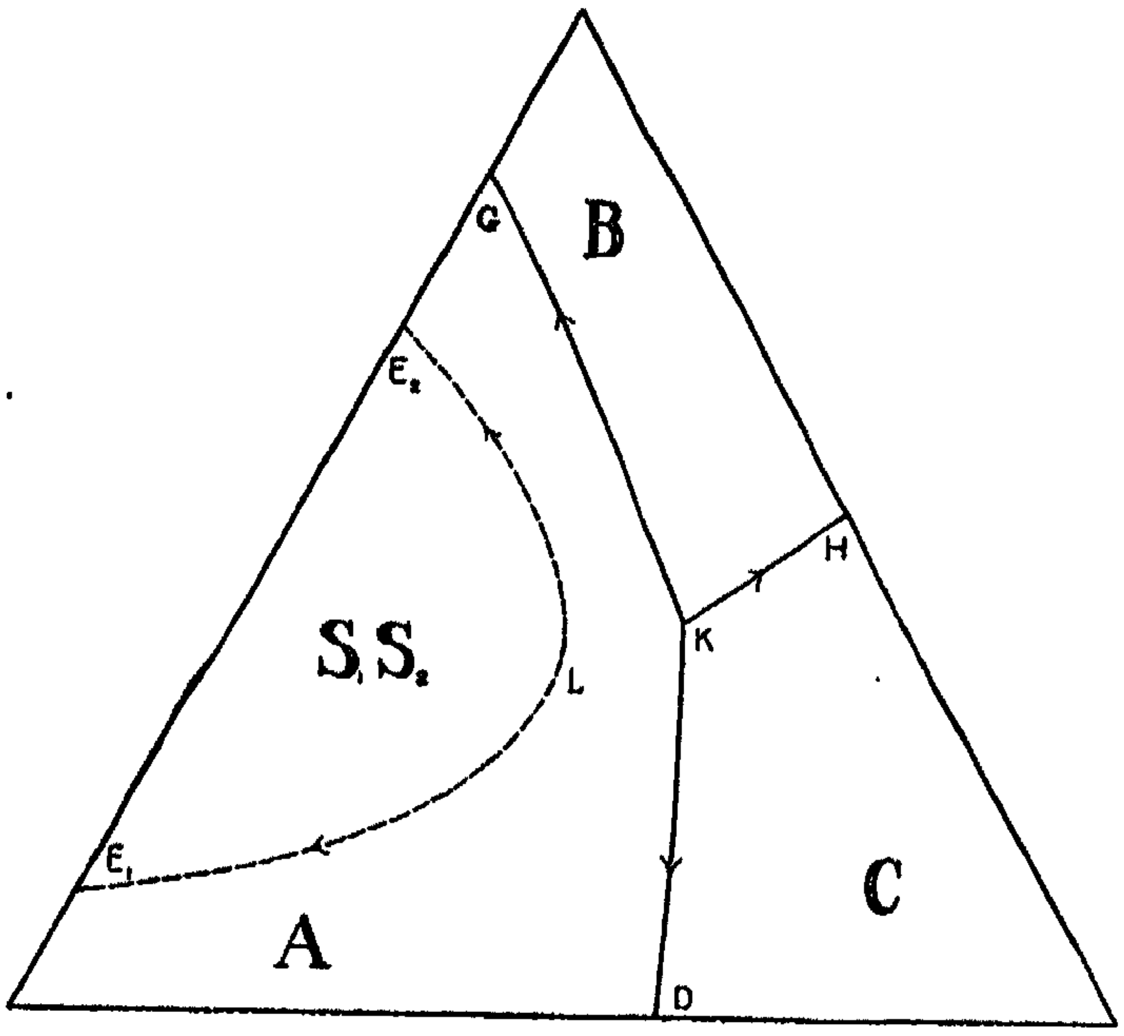

FIG. 3

shut off by E_1LE_2. This case is interesting because we no longer have the field in which A is solid phase divided into two parts; but more especially because this diagram probably represents one of the very common types of equilibrium. A system coming under this head can certainly be realized if we call naphthalene A, water B and alcohol C. It is probably to be realized with potassium nitrate, acetone and water as A, B and C respectively. While no one has yet shown experimentally that potassium nitrate and acetone form two liquid layers, there can be little doubt that this is the case—barring disturbances due to chemical action. It is well known that most salts will cause aqueous acetone to separate into two liquid layers at temperatures well below the boiling points of the mixtures and that some salts will do this with aqueous alcohol. In all such cases we have doubtless been dealing with systems coming under 1c, though of course the phenomena may be complicated in many instances by the melting point of A lying above the maximum critical temperature for mixtures of B and C, to say nothing of the minor disturbances due to the appearance of compounds. If the subject had been approached in the past with a view to determining complete diagrams we should probably be able now to predict why some salts should precipitate alcohol from aqueous alcohol at a given temperature while others do not.

We pass now to the cases under 2 where C dissolves in A with precipitation of B. Here we tread upon uncertain ground because it is not known whether this is compatible with the main postulate that B and C can not form two liquid layers by themselves. This question of precipitation I shall take up a little more in detail later in this paper and we can at any rate work out what the diagrams will be like if this condition is permissible.

No diagram is given for 2a because Fig. 1 will do perfectly if one imagines the lines E_1F_1 and E_2F_2 diverging instead of converging. With the same correction Fig. 2 will serve as a diagram for 2b. It is to be noticed that in these two cases, as well as in 2c, it is impossible for addition of C to go on making A and B less miscible indefinitely if only one pair of components A and B can form two liquid phases. Therefore in order for 2a, 2d and 2c to be realizable experimentally, it is essential that C shall dissolve in A with precipitation of B only over a limited range of concentrations and that then addition of C must increase the miscibility of A and B.

The diagram for 2c is given in Fig. 4. In this system we have two «secondary» quintuple points and a single «primary» one. At F_1 and F_2 we have A, B, two solutions and vapor; at N_1 and N_2, B, C, two solutions and vapor while at K there is one solution in equilibrium with A, B, C and vapor. Along E_1F_1 and E_2F_2 the phases are A_2, S_1, S_2 and vapor. Along F_1N_1 and F_2N_2, B, S_1, S_2 and vapor and along N_1L and N_2L they are C, S_1, S_2 and vapor. A, B, S_1 and vapor occur along F_1K; A, B, S_2 and vapor along F_2G; B, C, S_1 and vapor along N_1K; B, C, S_2 and vapor along N_2H and the four phases A, C, solution and vapor along KD. The temperature of F_1 and F_2 is lower than that of E_1 and E_2 and also lower than that of N_1 and N_2. This latter temperature is lower than that of L. The other temperature changes are described by the theorem of van Rijn van Alkemade so far as I know.

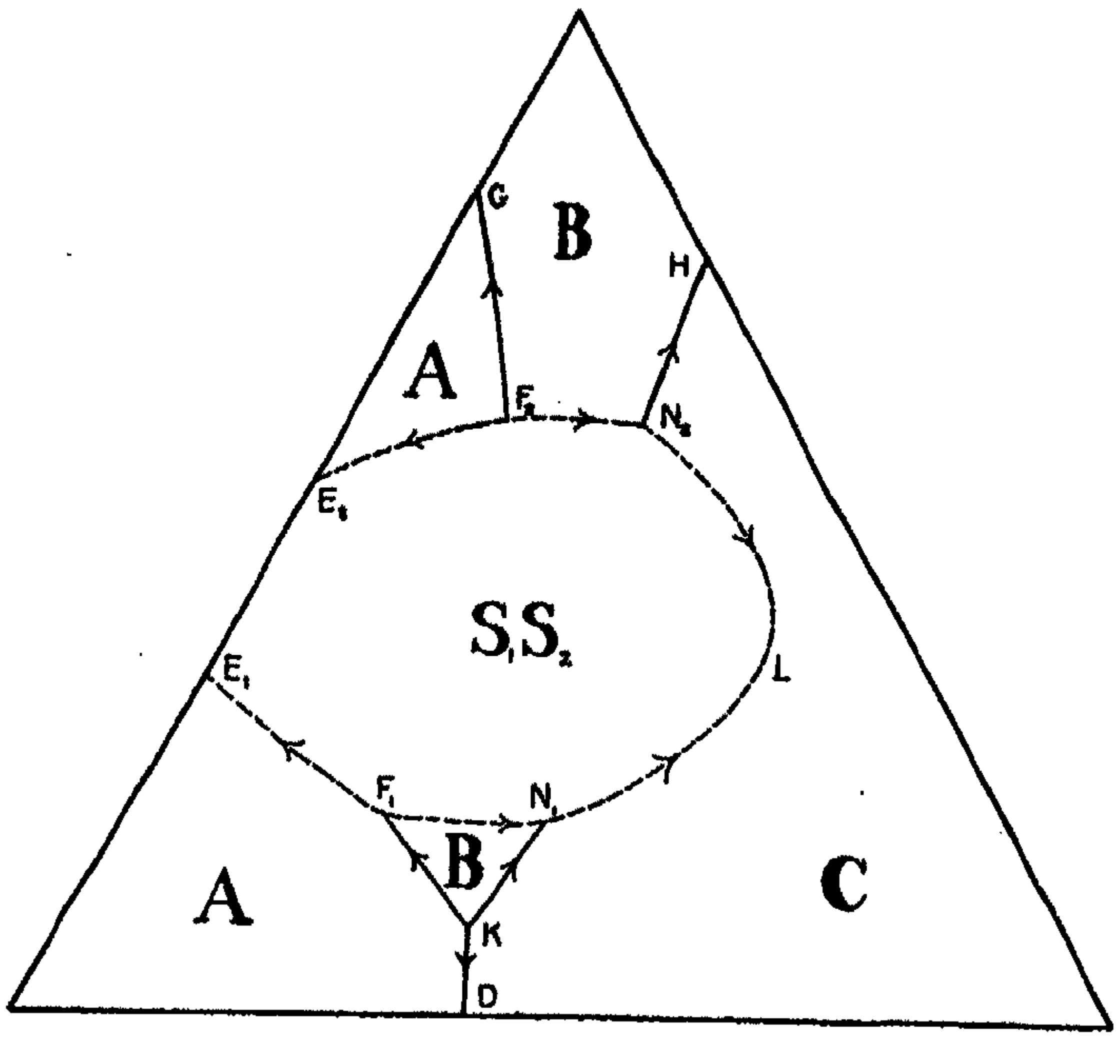

FIG. 4

The field for A as solid phase is made of two parts, one shut off by E_1F_1KD, the other by E_2F_2G. The field for B is also divided into two sections, one shut off by GF_2N_2H while the other is bounded by KF_1N_1K. C exists to the right of DKN_1LN_2H while the space enclosed by $E_1F_1N_1LN_2F_2E_2$ and the side of the triangle forms the field for two solutions and vapor.

When C dissolves in B with precipitation of A the question comes up anew whether this is compatible with there being only one pair of components which can form two liquid phases. Assuming temporarily that such a state of things is possible, there is but one system which can exist, A and C being the solid phases in equilibrium at the «secondary» quintuple point. The diagram for such a system would differ from Fig. 1 in that the lines E_1F_1 and E_2F_2 would diverge instead of converge and that the temperature would rise in passing from E_1 and E_2 to F_1 and F_2. No system is possible corresponding to Fig. 2 or Fig. 4 because the temperature of E_2 is higher than that of G. Since the temperature falls in passing along the boundary curve running from G and rises along the one running from E_2 it is obvious that these two curves can never intersect. It will not be necessary to consider the changes introduced by assumptions in regard to the place at which systems coming under classes 2 and 3 change into class 1. Since such details introduce no theoretical difficulties, they present no interest until there are experimental data illustrating them.

By glancing back over the four cuts, one sees at once the relation between three-component systems where two liquid phases are impossible and those in which one pair of components can be treated as partially miscible liquids. The latter are derived from the former by addition of the curves for the two liquid phases, which may cut none, one or two of the regular boundary curves. Looked at in this way one would be inclined to take 1c as the first case, in which the development of the two liquid phases is more or less rudimentary ; 1a, 1b, 2a, 2b, 3a would then result from a more marked tendency to separate into two liquid phases while 2c would be typical of all the remaining cases until the point L reaches the side of the triangle when we have two pairs of components forming two liquid phases.

This brings us to subdivision II including all systems in which A and B and B and C form two liquid phases while A and C do not.

The diagram for a system with A and C as the solid phases at the one «secondary» quintuple point, as required for 4a, is shown in Fig. 5.

At F_1 and F_2 we have a «secondary» quintuple point with A, C, two solutions and vapor as the phases; at K a «primary» quintuple point with A, B, and C in equilibrium with solution and vapor.

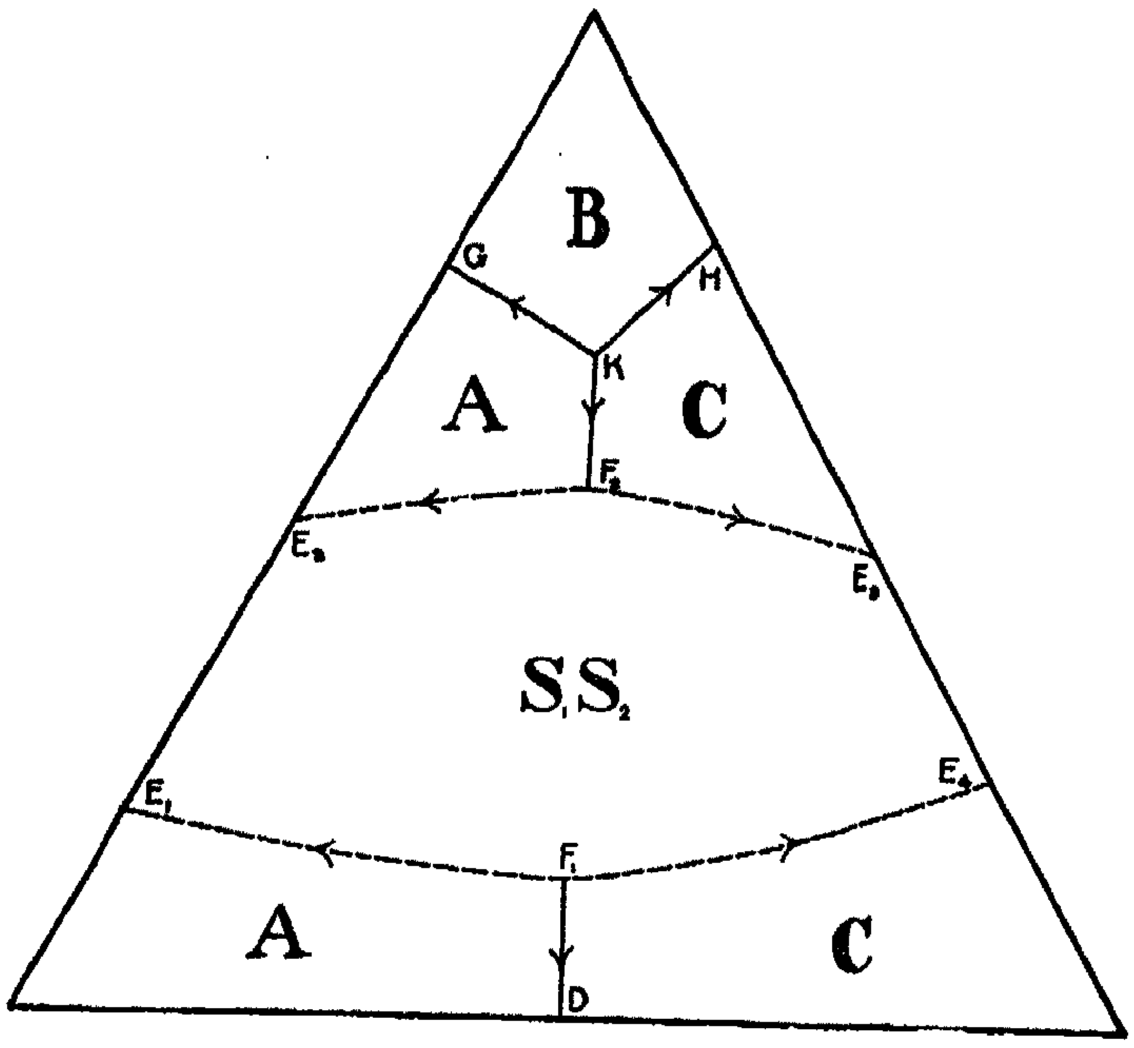

FIG. 5

The monovariant systems represented in the diagram are A, S_1, S_2, solution and vapor along E_1F_1 and E_2F_2; C, S_1, S_2 and vapor along E_4F_1 and E_3F_2; A, C, S_1 and vapor along F_1D; A, C, S_2 and vapor along F_2K; A, B, solution and vapor along KG and B, C, solution and vapor along KH. The temperature rises in all cases as one passes along the boundary curves to the sides of the triangle and also from K to F_2. The fields for A as solid phase are marked off by E_1F_1D and by E_2F_2KG; that for B is limited by GKH. The detached portions of the field for C are shut off by HKF_2E_3 and by E_4F_1D while two solutions and vapor can exist only in the strip between $E_1F_1E_4$ and $E_2F_2E_3$. Naphthalene, water and sulfur would give a diagram like this one.

Under 4b we group systems with one «secondary» quintuple point, A and B being the solid phases. The diagram for this case is shown in Fig. 6. At F_1 and F_2 the five phases are A, B, two solutions and vapor; at K we have A, B and C in equilibrium with solution and vapor. Along E_1F_1 and E_2F_2 there is the monovariant system, A, S_1, S_2 and vapor while B, S_1, S_2 and vapor exist along F_1E_3 and F_2E_4. A and B coexist with S_1 and vapor along F_1K and with S_2 and vapor along F_2G. Solution and vapor are in equilibrium with A and C along KD and with B and C along KH. The only temperature change of interest is that along E_3F_1 and E_4F_2 where there is a rise as one passes away from the side of the triangle. The fields for A, B and C as solid phases are in this case, as in those which

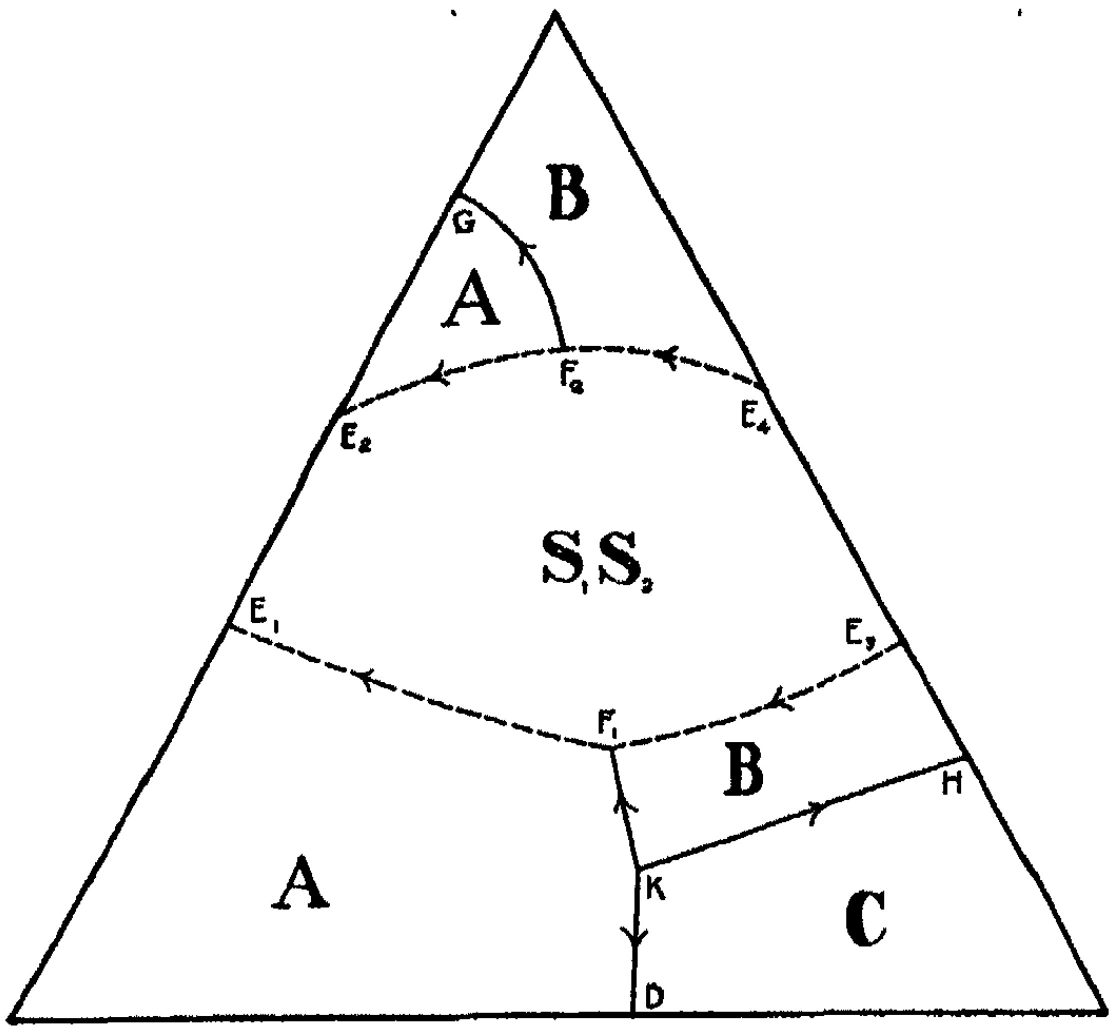

Fig. 6

have been and are yet to be considered, exactly what they would be if no second liquid phase were possible minus the strip within which two solutions and vapor occur. If one were to study a system in which A denoted naphthalene, B stood for water and toluene was the third component one would get a diagram resembling Fig. 6 in all except relative proportions.

In the preceding paper it has been pointed out that with phenol, water and naphthalene as A, B and C respectively, there are two

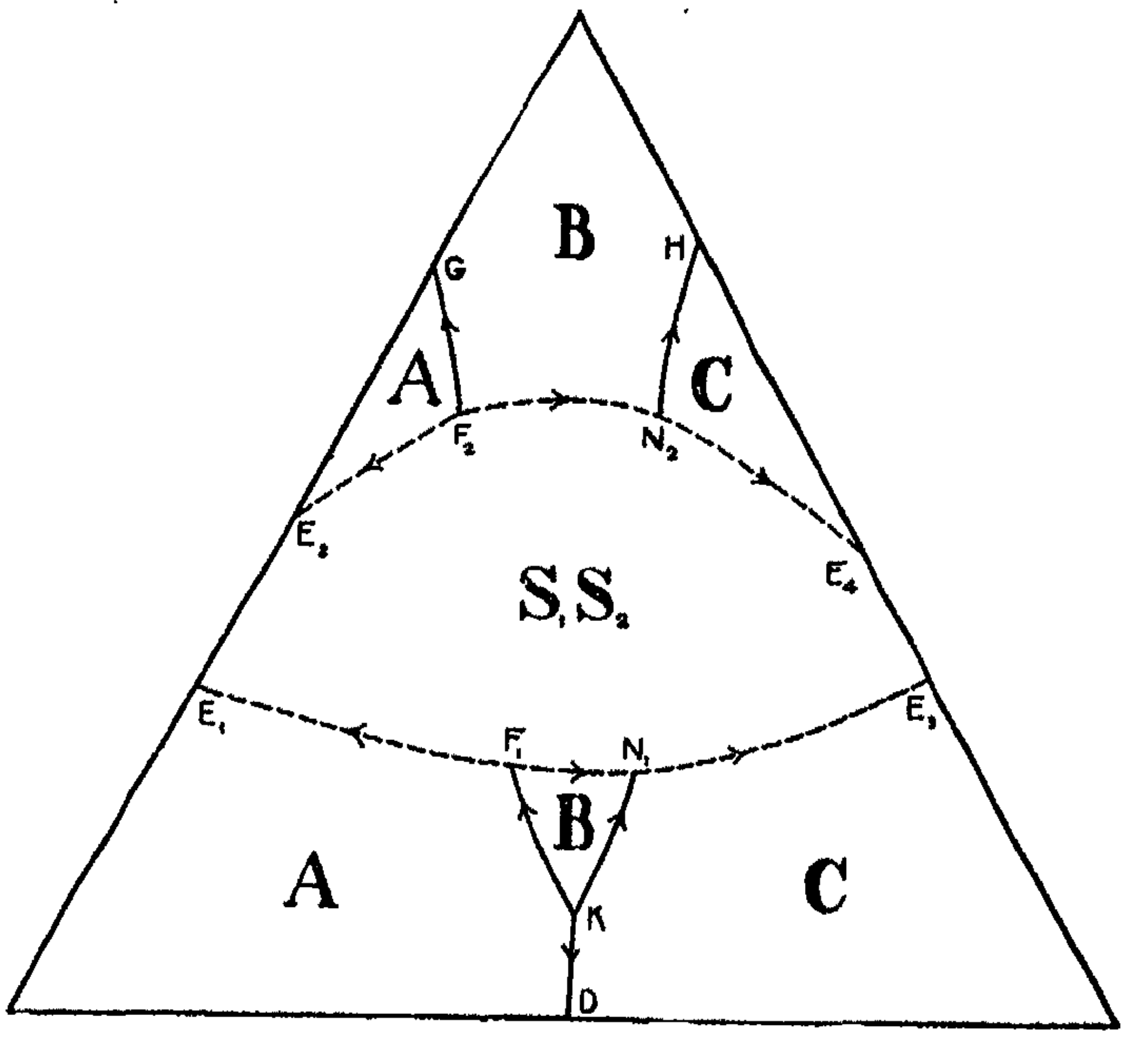

FIG. 7

quintuple points with two liquid phases. The diagram for this case, 4c, is given in Fig. 7. At F_1 and F_2 the phases are A, B, two solutions and vapor; at N_1 and N_2 they are B, C, two solutions and vapor while at K we have, as always, A, B, C, solution and vapor. The monovariant systems are A, S_1, S_2 and vapor along E_1F_1 and E_2F_2; B, S_1, S_2 and vapor along F_1N_1 and F_2N_2; C, S_1, S_2 and vapor along N_1E_3 and N_2E_4; A, B, S_2 and vapor along F_2G; B, C, S_2 and vapor along N_2H; A, B, S_1 and vapor along F_1K; B, C, S_1 and vapor along N_1K and A, C, solution and vapor along KD. The temperature rises along the boundary curves to the sides of the triangle; from F_1 and F_2 to N_1 and N_2 and from K to both these points. This is the first instance of a system in which the fields for all three components are cut into two portions. The field for A is limited by E_1F_1KD and by E_2F_2G; that for B by GF_2N_2H and KF_1N_1K; that for C by HN_2E_4 and by E_3N_1KD while two solutions and vapor can exist only between $E_1F_1N_1E_3$ and $E_2F_2N_2E_4$.

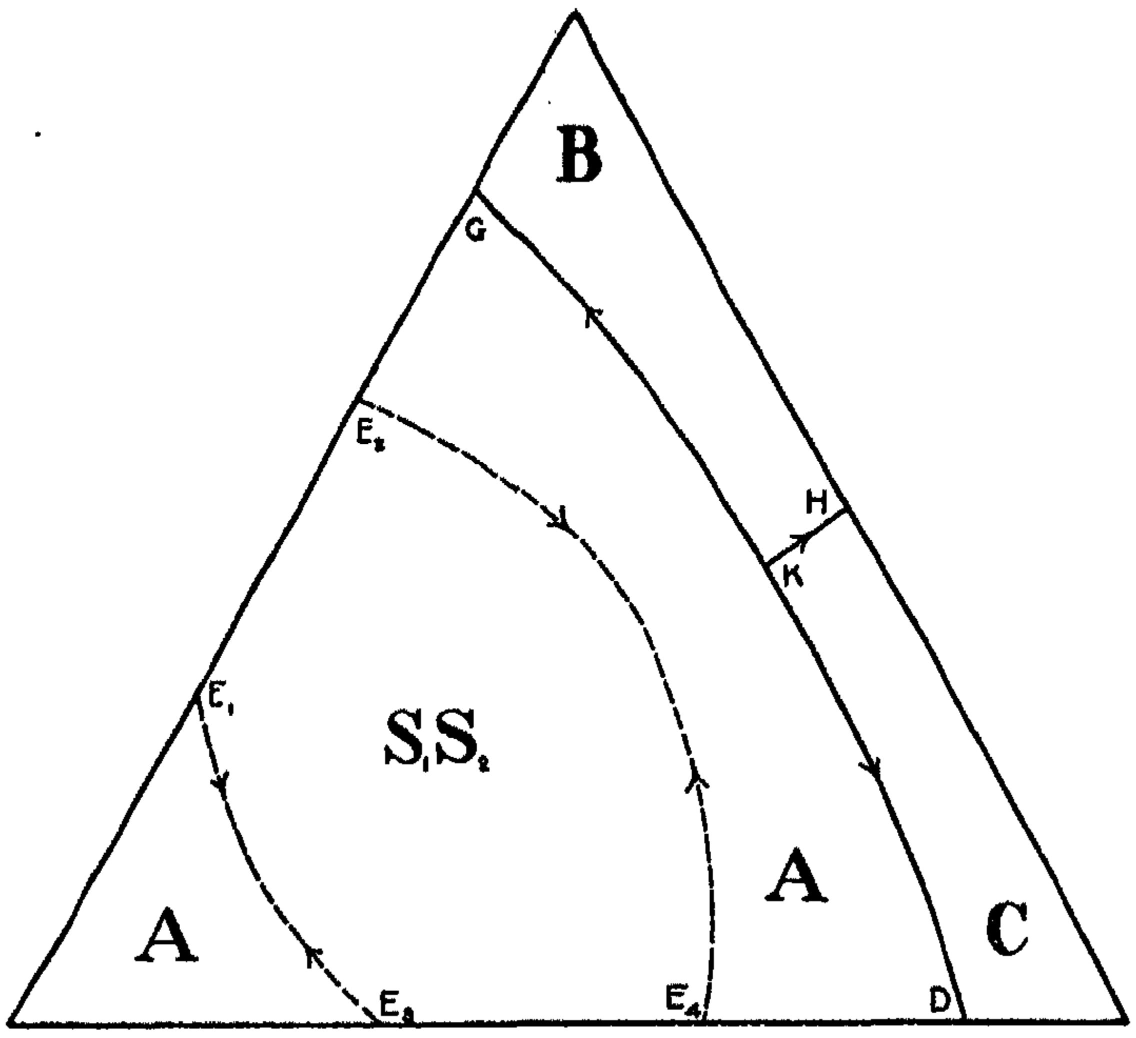

FIG. 8

Passing to subdivision III in which it is assumed that there are two pairs of components which can form two liquid phases, A and B, A and C, we find that there is only one case that needs consideration. This is the one called 5a, in which there is no « secondary » quintuple point. The diagram for this case is Fig. 8. The cut needs little comment. Two solutions and vapor occur between E_1E_3 and E_2E_4 while A is solid phase in all the rest of the area to the left of GKD. In all probability there is a temperature maximum somewhere on E_1E_3 and E_2E_4 but there are no measurements to prove this and there is therefore nothing to be gained by discussing the significance of the concentrations at this point. This is a question which I hope to take up before long. Systems coming under this head would be water, chloroform and toluene or water and any two esters always excepting methyl acetate.

It is always possible to have a system which could be classified under subhead 5 in which the solid phases at the «secondary» quintuple point should be A and C; but this would not really be a new case. It would be 4b over again with what had been B masquerading as C and *vice-versa*. A diagram analogous to 4c is impossible for the same reason that there was nothing under subhead 3 corresponding to 2c.

Throughout the discussion of systems in which two pairs of components can form two liquid phases, it has been assumed tacitly that the field for two solutions and vapor is never composed of two detached portions. While this is true in the vast majority of cases, there may be exceptions. If the temperature at which A and B become consolute is low and the melting point of C is high, the two solutions in which A and B predominate respectively may become identical before C appears or before it begins to melt under the solutions. Phenol and water or benzoic acid and water would do excellently for A and B while C would have to be some high-melting substance addition of which changed the consolute temperature for A and B but slightly. The diagram for such a state of things is not given but may be derived by supposing E_1E_3 and E_2E_4 to break at some point giving two hoop-shaped curves $E_1L_1E_3$ and $E_2L_2E_4$.

We can now pass to systems in which all three pairs of components can form two liquid phases and we begin with the case in which three liquid phases can not exist simultaneously. The diagram is given in Fig. 10. At F_1 and at F_2 there is a «secondary» quintuple point with A, C, two solutions and vapor in equilibrium while at K the three components, solution and vapor form the five phases. The monovariant systems are A, two solutions and vapor along E_1F_1 and E_2F_2; C, two solutions and vapor along F_1L and F_2L; A, C, S_1 and vapor along F_1D; A, C, S_2 and vapor along F_2K; A, B, solution and vapor along KG; B, C, solution and vapor along

KH while the component C can exist in equilibrium with vapor and a second pair of solutions along E_4E_5 and E_3E_6. The temperature rises along F_1D, F_1L, F_2L and in all directions from K. Along E_4E_5 and E_3E_6 the temperature rises as we pass from the sides of the triangle so that there is a maximum somewhere in the middle of the curves. Nothing can be told about the temperature changes along E_1F_1 and E_2F_2 until it is known whether, in any given case, C is more soluble in A than in B or *vice-versa*. The field for A consists

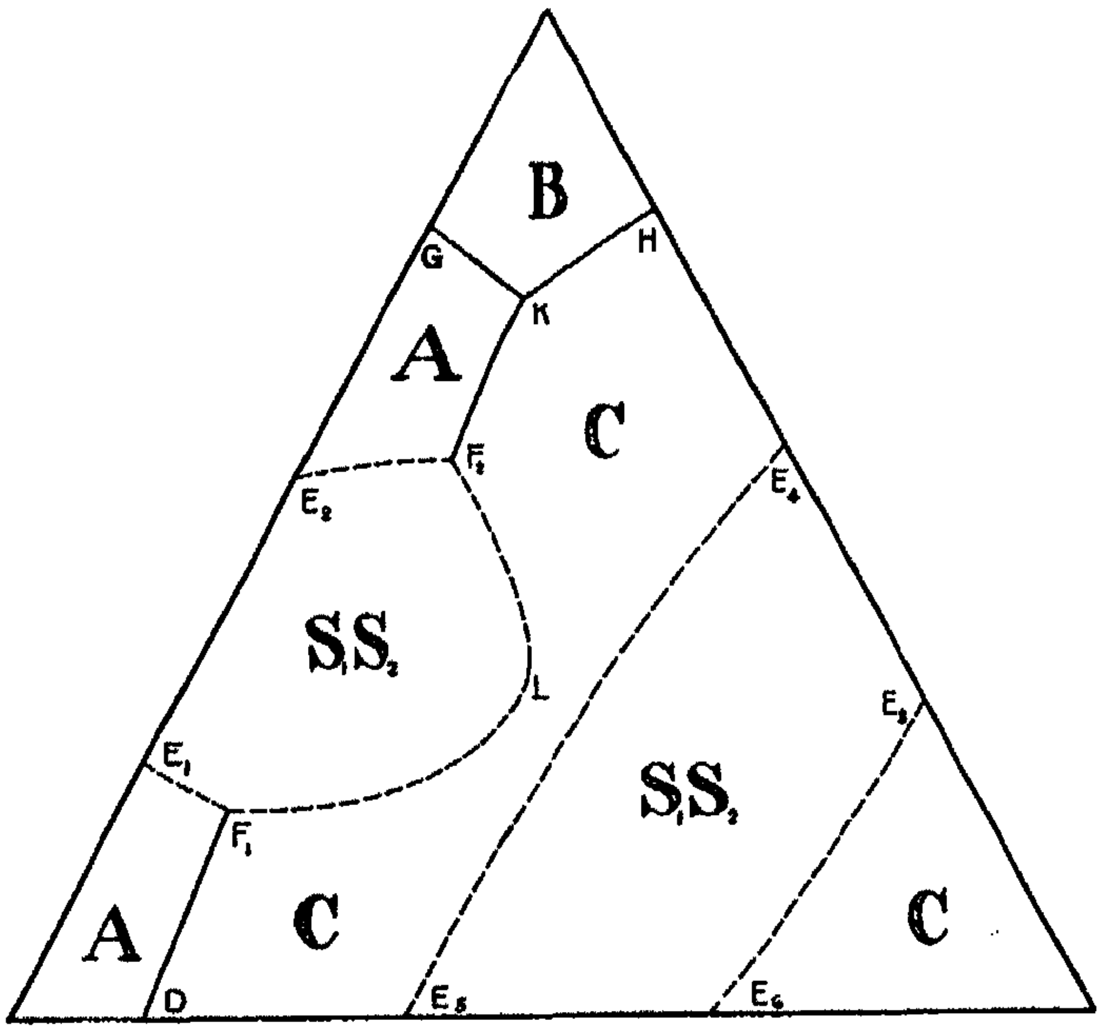

FIG. 10

of two parts, one cut off by E_1F_1D; the other by E_2F_2KG. The field for B lies above GKH. One of the fields for C lies to the right of E_3E_6 and the other between DF_1LF_2KH and E_4E_5. Two solutions and vapor can exist within $E_1F_1LF_2KE_2$ and between E_4E_5 and E_3E_6. Barring chemical action this system could probably be realized with phenol, water and sulfur as A, B and C respectively.

We have next to consider the case in which three liquid phases can coexist in stable equilibrium. The schematic diagram for sulfur, water and toluene is given in Fig. 11, sulfur being A, water B and toluene C.

At X_1, X_2 and X_3 there is a quintuple point[1] with solid A, three solutions and vapor as the five phases. To distinguish the three liquid phases we will designate by S_1 the one containing an excess of C ; by S_2 the one with an excess of B and by S_3 the one with an excess of A. We have A, S_1, S_2 and vapor along X_1F_1 and X_2F_2 ; A, S_1, S_3 and vapor along X_1E_6 and X_2E_5 ; A, S_2, S_3 and vapor along X_2E_2 and X_3E_1 while three solutions and vapor exist along X_1L_1, X_3L_1 and X_2L_2. At temperatures lower than that of X_1, X_2 and X_3 the third solution disappears and at F_1 and F_2 we have B appearing as solid phase forming the «secondary» quintuple point with A, B, two solutions and vapor as the five phases. The monovariant systems are A, S_1, S_2 and vapor along X_1F_1 and X_2F_2 ; B, S_1, S_2 and vapor along F_1E_3 and F_2E_4 ; A, B, S_1 and vapor along F_1K ; A, B, S_2

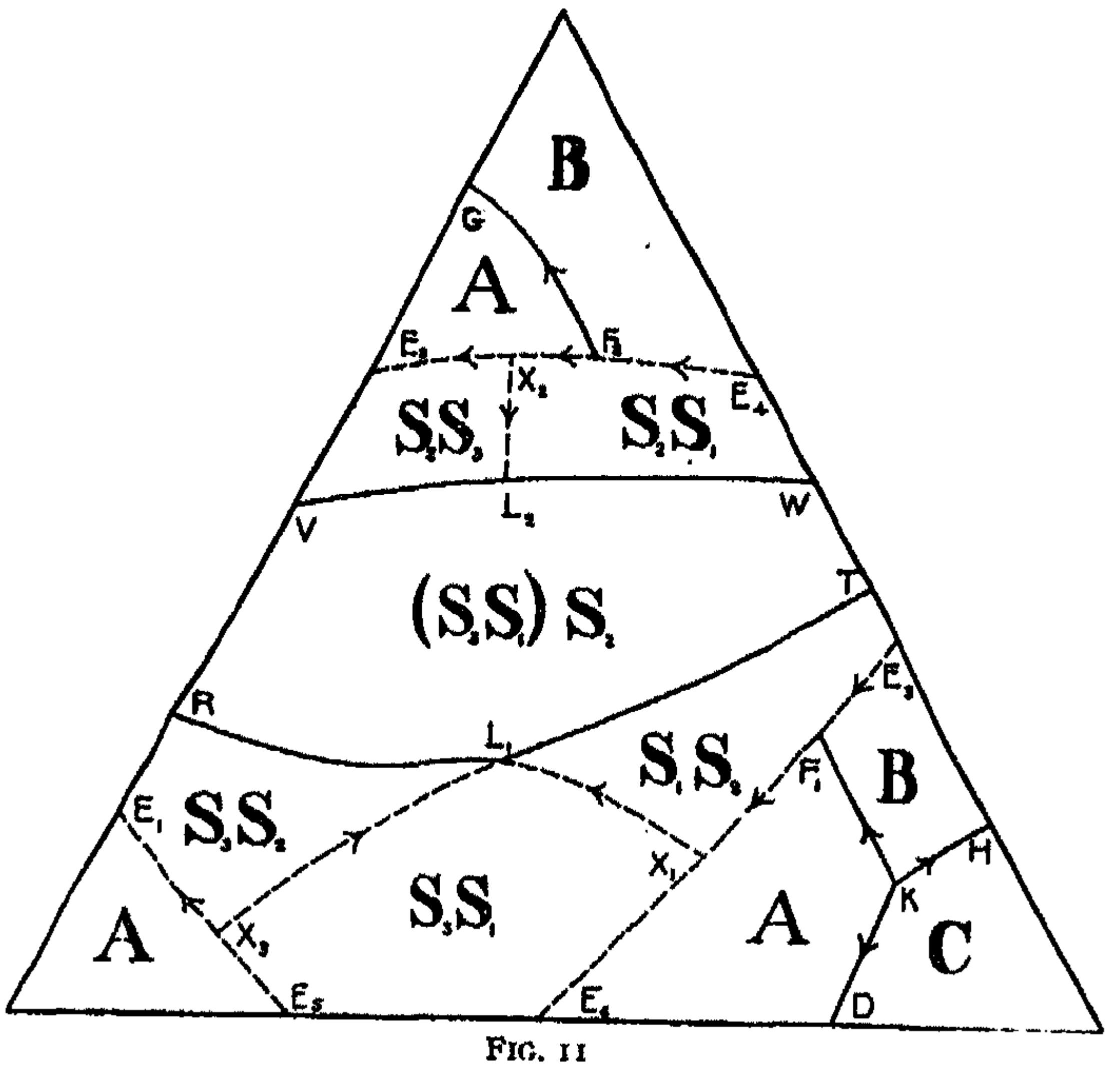

FIG. 11

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[1] This might be called a «tertiary» quintuple point.

and vapor along F_2G. At K we have a «primary» quintuple point with A, B and C in equilibrium with solution and vapor. The curves for the monovariant systems meeting in K are lettered as in all the preceding cases and need no special enumeration. The temperature rises continuously from E_3 and E_4 to X_1 and X_2; it rises from X_1, X_2 and X_3 to L_1 and L_2; it rises from X_2 and X_3 to E_2 and E_1 and it is impossible to predict without further data whether it rises or falls from X_1 and X_3 to E_6 and E_5. To answer this question one must know whether the consolute temperature for water and toluene is higher or lower than the corresponding temperature for water and sulfur. The changes of temperature for the boundary curves along which there is only one solution are in accordance with the theorem of van Rijn van Alkemade. The solutions called S_3 and S_1 become identical at the temperature of L_1 and L_2; above this point it is not possible to have more than two solutions in equilibrium. The temperature range for three solutions and vapor thus lies between X_1X_2 and X_3 as a lower limit and L_1 and L_2 as an upper limit. For convenience in describing the fields for the divariant systems, I have marked this upper limit, RL_1T and VL_2W being supposed to be the isotherm through L_1 and L_2.

The field for A as solid phase in equilibrium with solution and vapor consists of three portions, one for each solution. The limiting curves are $E_1X_3E_5$, $E_2X_2F_2G$ and $E_6X_1F_1KD$. The component B is found in two distinct fields, one shut off by GF_2E_4 and the other by E_3F_1KH. The single field for C extends only as far as HKD. The solutions S_1 and S_3 can exist in equilibrium with vapor within the limits of $E_5X_3L_1X_1E_6$. Mixtures corresponding to points within the fields bounded by $E_1X_3L_1R$ and $E_2X_2L_2V$ will separate into solutions S_3 and S_2; the fields for S_1 and S_2 run to $E_3F_1X_1L_1T$ and $E_4F_2X_2L_2W$, while in the strip between RL_1T and VL_2W are to be found two solutions which may be called S_3 and S_2 or S_1 and S_2 at pleasure since there is no longer a distinction between S_3 and S_1.

It is safe to say that the general form of the diagram for sulfur, water and toluene is shown in Fig. 11 provided the whole diagram is realizable experimentally. If one took other combinations of three components, one could get other forms of Fig. 11. In this particular case we have the consolute temperature for A and C lower than that for

A and B or B and C. This shows at once two other assumptions that might have been made. From this single diagram anyone who is interested in the subject can work out the others and it would be useless waste of space to give them here. There is one point which may occur in any of the cases discussed and which therefore deserves a moment's attention. I refer to the possibility of a critical temperature being reached. With a low melting salt, acetone and water there would be no difficulty in realizing the whole diagram; but with such a salt as sodium or potassium chlorid this would probably be impossible owing to the vapor phase becoming identical with one of the liquid phases at some temperature. This would be shown in the diagram by the boundary curve for A, two solutions and vapor not reaching to the side of the triangle. The field for two solutions and vapor would then be enclosed by the boundary curve in question and the part of the isotherm connecting the open ends.

The conditions of equilibrium for three-component systems are so markedly functions of the relative miscibilities that it is only natural to inquire whether there is any regularity to be noticed between precipitation and solubility. The historical development of the subject is very interesting. It has long been known to the qualitative chemists, inorganic and organic, that if one adds to a solution a liquid in which the solute does not dissolve, the latter is apt to be precipitated. This seemed so natural that it attracted no attention. Here precipitation was a question of solubility only. When the quantitative chemists took up the question of changes in solubility, they naturally approached the subject from the point of view of the dissociation theory. Nernst[1] showed that, judging from analogy, there should be a decrease in solubility if one of the dissociation products of the solute was added to a saturated solution. This proved to be the case in a large number of instances, the only exceptions which were studied being explained by assuming the formation of compounds in solution. So far there was nothing to which anyone could object seriously. The next step was to state that the solubility of a salt which crystallized in the anhydrous state from water could be diminished only by addition of the undissociated solute or one of its dissociation products. This statement is

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[1] Zeit. phys. Chem. 4, 372 (1889).

not in accordance with facts; but this does not seem to have troubled people very much. The attempts to refer all changes of solubility to the same cause have failed and it will be advantageous to recognize distinctly that we are dealing with two sets of phenomena. In one case the change of solubility is due to the relative miscibility of the two components under consideration. In the other it is a question of a change of dissociation. There is no need of rejecting Nernst's explanation of the effect of silver nitrate upon the solubility of silver bromate because the same explanation can not be applied to the precipitation of potassium nitrate by alcohol. It would be equally absurd to conclude from the experiment with potassium nitrate and alcohol that silver bromate is practically insoluble in fused silver nitrate. While it is easy to see that no addition of dissociation products takes place in many cases, as in the precipitation of potassium chlorid by alcohol, where the two substances have no element in common, there is no obvious reason why the effect due to relative miscibility should not always exert an influence. For the present, therefore, we must assume that that is the case. Since potassium chlorid and sodium chlorid are miscible in all proportions when fused we should naturally conclude that there would be a tendency for each to increase the other's solubility in water. This would be counteracted to a greater or less extent by the fact of the two having a common dissociation product in aqueous solution. Since we have no absolute quantitative theory for the precipitation of one salt by another, it is impossible to tell experimentally whether there is an effect due to the mutual solubilities of the salts when fused. We can answer the question better in another way by considering under what conditions we get a maximum effect due to the solubility phenomena and then seeking out cases in which this factor is of such importance as to be recognized at sight. The solubility of substances in gases is so slight at ordinary pressures that the very existence of this phenomenon is not yet generally admitted. With solids which do not form solid solutions we should expect to find the effect of mutual solubility diminishing in intensity as the temperature falls below the eutectic tempertature for the two solids. The maximum effect is therefore to be expected when at least one of the substances in question is a liquid. This is the case which led the qualitative chemist to his incomplete generalization that the change of solubility is a question of the miscibility of the solute and the third component. This is the case which the quantitative chemist overlooked in making his incomplete generalization that change of solubility is a question of the concentration of dissociation products. It is safe to conclude that if we add to a saturated salt solution a liquid having an ion in common with the salt, we shall first find a decrease in the solubility of the salt. If the salt is soluble in the liquid we shall eventually have this effect predominating and the concentration of the salt will increase. This has been observed experimentally. Addition of sulfuric acid in small quantities decreases the solubility of lead sulfate; but this salt is readily soluble in concentrated acid. Engel[1] has found a minimum solubility for nitrates in aqueous nitric acid and there are other similar cases[2]. In these cases the solvent action of the liquid outweighs at length the precipitating effect due to the common ion. We can get much the same result with two solids by merely changing the temperature at which the experiment is performed. At 20° addition of potassium nitrate to a saturated solution of potassium chlorid decreases the solubility of the latter. If we are working at the temperature of the eutectic mixture of the two salts, addition of potassium nitrate to a solution saturated with respect to potassium chlorid causes the latter to go into solution until the ratio of potassium chlorid to water becomes infinity. Whether the first addition of potassium nitrate causes a precipitation of potassium chlorid is not known. This makes clear that we have handicapped ourselves in the past by assuming that the behavior of one set of substances under one set of conditions was characteristic of the behavior of all substances under all conditions. This is not in any way surprising. Most progress is made by generalizing from one instance and modifying the conclusion in the light of the facts. The more strikingly successful the generalization, the more difficult it is to modify it. In the particular instance under discussion, the habit of most physical chemists of considering dilute solutions alone has precluded the possibility of seeing the subject as a whole.

[1] Cf. Ostwald. Lehrbuch I, 1081.

[2] Ditte. Comptes rendus, **123**, 1281 (1896).

If the views which I have just put forward be sound, the following predictions should hold. The solubility of a solid should be affected but slightly by the addition of another solid having no common dissociation product. The solubility should in general be increased if the two solids are miscible in all proportions when fused and should be decreased if the two substances are practically nonmiscible when fused[1]. These effects should increase in intensity as the temperature of the experiment approaches the melting point of the more fusible substance. It is known that these predictions are verified in some cases. McIntosh[2] has shown that ice precipitates benzene from mixtures of benzene and alcohol at temperatures below zero. Whether these predictions hold true under all circumstances is quite another matter. There may easily be other factors coming in. We do not know why the solubility of a substance in a mixture of two solvents should sometimes be greater or less than the solubility in either of the pure solvents yet such cases are known. There is no place in any theory for such systems as diethylamin and water in which the two components are miscible in all proportions below a certain temperature and separate into two liquid layers at a higher temperature. For that matter we are completely at a loss to account for decreasing solubility with rising temperature and yet that is a very common phenomenon with liquids. It is true that a decrease of solubility with rising temperature connotes other properties and connotes them quantitatively; but that is a very different thing from an explanation of the occurrence.

All that I have tried to do in these last few pages is to show that there are at least two factors which may have to be taken into account, the miscibility phenomena and the dissociation phenomena. The latter are very important in the equilibria between gases and solids where there is no liquid phase and in certain cases of equilibrium in solutions. The former phenomena occur in all solutions but the effects are often negligible at certain temperatures.

There has been given in this paper a graphical summary of the equilibria in three-component systems when one pair, two pairs and

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[1] This would seem to make cases 2 and 3 impossible unless two of the components had a common dissociation product.

[2] Jour. Phys. Chem. 1, 474 (1897).

three pairs of the components can form two liquid phases. The treatment does not include a study of the isotherms. In addition there is a discussion of some of the factors affecting changes of solubility.

Cornell University; July, 1897.

NEW BOOKS

Eine Kritik der Nernstschen thermodynamischen Auschauungen, *Eine Antwort auf die Kritik meines Buches. A. H. Bucherer. 31 pages. Freiberg i. S., Craz und Gerlach, 1897. Price 60 Pfg.* The author complains of being misrepresented by Nernst in the latter's criticism[1] of his *Grundzüge* and considers it his duty in return to submit the theories of Nernst to a thoroughgoing *Gegenkritik.* The tone of this publication may best be judged of from a citation or two :—

«Nernst's position is characterized by his unconcealed conviction that ideas which do not agree with his own are *Eo ipso* absurd» (p. 5).

«Everything that Mr. Nernst says about the work done by chemical processes is erroneous and contradicts thermodynamics» (p. 11).

«An exact general deduction of electrochemical forces was first rendered possible by the introduction of the vapor tensions of the metals by myself, *etc.*» (p. 6).

The proper way, it seems, to attack the problems of electrochemistry is by means of ‹a correct energetics›. As interpreted by our author this science requires that «if a solid phase be in equilibrium with a partially decomposed vapor, the solid must also be in the same state of decomposition ; and moreover the partial pressures of the products of decomposition in the solid must be exactly equal to the corresponding partial pressures in the vapor». As an example of the application of these principles may be quoted :—

«If solid silver bromid be brought into a vacuum, a vapor will be given off containing silver bromid molecules, free bromin and an equivalent quantity of free silver vapor. . . . Thermodynamics

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[1] Zeit. Electrochemie, **3**, 435 (1897).

compel us to conclude that solid or melted silver bromid consists of these same molecules *and no others*; it is consequently *obvious that there can be no such thing as charged ions.* Mr. Nernst ascribes this conclusion to my incompetence!»

Ions being thus inconsistent with «a correct energetics», there still remains the question of the freezing points, *etc.* of electrolytic solutions. If common salt be dissolved in a large quantity of water, the value of *n/N* as calculated from the freezing point is just twice that expected from the composition of the solution. Van 't Hoff and Arrhenius ascribed this discrepancy to the existence of two ions in place of one molecule of salt, E. Wiedemann to a polymerization of the water to double molecules (H_4O_2), while Bucherer refers it to the «association» of part of the water with the salt to form a hydrate, and thus «escapes the difficulties of the hydrate hypothesis» and «restores the electrolytes to the category of ordinary chemical substances».

The writer regrets that in his review of the *Grundzüge* in the last number of this Journal, he misstated Mr. Bucherer's position with respect to this important point. In the book in question Wiedemann's hypothesis is quoted in full, but no refutation is offered, nor is there any hint that Wiedemann's conclusion is «in conflict with a correct energetics». This omission, and the total absence of the vigorous denunciation with which the author is wont to overwhelm those who differ from him, led to the regrettable misapprehension. *W. Lash Miller*

La Continuité des Etats gazeux et liquide. *J. D. van der Waals. Traduit de l'allemand et annoté par MM. Dommer et Pomey. Large 8vo, xvi and 280 pages. Georges Carré; Paris.* Van der Waals's very interesting work on the continuity of the gaseous and liquid states is now accessible in a French rendering, as well as in the original Dutch and in the German and English versions of Roth and of Threlfall and Adair. The present French text is a translation from the German. The character of the work itself—in its development of the Waalsian equation, and of the corresponding theory of continuity and of the thermodynamic properties of fluids—is too well known to need comment; we need merely to record with pleasure the appearance of another translation. An interesting feature of the present edition is a preface by E. Sarrau, which gives an uncommonly well written review of the history of the theory, from the dicoveries of Regnault and of Natterer that under low pressures the densities of gases usually rise more rapidly than their pressures, while under high pressures the contrary is the case, to the observations of Andrews upon the critical phenomena, the development and application of the Waalsian theory, the location of the vaporization isotherm by Maxwell and by Clausius and, finally, to the elaboration of the theory of corresponding states. Sarrau's attitude towards the equation of van der Waals is, moreover, a sensible one; he realizes that this equation is an approximation, whose importance lies in exhibiting in broad outlines the relations which subsist in a great class of natural phenomena. «For through such syntheses are physical theories developed.» The volume is concluded by an extended series of notes upon difficult points in the text, and by two articles by Guye and by Mathias on recent work in the subject. The mechanical make-up of the book is good. In preparing this careful edition of an important work Messrs. Dommer and Pomey have rendered a real service to science.

J. E. Trevor

Physical Chemistry for Beginners. *Ch. M. van Deventer. 167 pages. W. Engelmann; Leipzig, 1897. Price 3.50, bound 4.10, marks.* Van 't Hoff, in his lectures on chemistry at the Amsterdam University, broke each chapter of the subject into two separate parts, the one constructing the systematic side upon a wholly experimental basis, and the other developing from this material the principles of the science. For the theoretical part of this instruction no text book was available, until, finally, the present little work was written by his assistant van Deventer to meet the exigencies of the situation. In his preface to the volume van 't Hoff gives this bit of laboratory history, and emphasizes the importance of having, for the use of beginners, a brief and simple treatise upon the principles of physical chemistry. The book treats the laws relating to composition, the behavior of gases, molecular and combining weights, general thermochemistry, the theory of normal and of electrolytic solutions, color phenomena and the periodic law. Taken all in all it seems to be admirably adapted to the purpose which it is intended to subserve. *J. E. Trevor*

Experimental-Untersuchungen ueber Elektrizität. *Michael Faraday. III. bis V. Reihe (1833), No.* 86, *104 pp, 1.60 marks. The same, VI. bis VIII. Reihe (1834), No.* 87, *180 pp, 2.60 marks. Ostwald's Klassiker der exakten Wissenschaften; W. Engelmann, Leipzig, 1897.* Faraday's electrochemical researches are indispensable to the modern electrochemist; their reappearance in Ostwald's neat *Klassiker* edition is accordingly to be greeted with much satisfaction. They were begun in No. 81 of the series, this Journal **1**, 373, and are continued in the present little volumes. All are carefully edited and annotated by von Oettingen. *J. E. Trevor*

Jahrbuch der Elektrochemie. 1896. *W. Nernst and W. Borchers. Large 8vo. Vol. III, 359 pages. W. Knapp; Halle, 1897. Price 14 marks.* In the preparation of this volume Nernst and Borchers have received the assistance of Küster and of Elbs, Küster reviewing the work in electrochemical analysis while Elbs takes the primary batteries, the accumulators and the organic syntheses for his share. This year 72 pages are devoted to pure electrochemistry and 260 pages to the technical developments. The scientific part of the subject is treated under the following heads: electrolytic conductivity and dissociation; electromotive forces; polarization and electrolysis; apparatus; dielectric measurements; electrochemical analysis. The headings for applied electrochemistry are: primary batteries; accumulators; furnaces; metallurgy; inorganic and organic preparations; bleaching and disinfecting. The volume closes with a list of books on chemistry published during the year.

From the point of view of interest the volume is an improvement over that of the year before. We have the work of Luther and of Löwenherz on solutions containing alcohol, Lovén's paper on concentration cells, the discussions of the single potential differences and the work of Nernst and his pupils on dielectric constants. In the technical part we have a discussion by Borchers of the attempts to obtain electricity direct from coal and a sketch of electric furnaces while all the work in organic preparations is of the highest importance. There is but one serious drawback. The volume should appear in March instead of July. *Wilder D. Bancroft*

Le Four Électrique. *H. Moissan. Large octavo, viii and 385 pages. G. Steinheil; Paris, 1897. Price 15 francs.* **Der Elektrische Ofen.** *The same. viii and 361 pages. Authorized German Edition, translated by T. Zettel. Fischer's technologischer Verlag, M. Krayn; Berlin W, 1897.* In this book Moissan has brought together the papers on the electric furnace which he has published during the past five years. We have first a description of the furnace, then a discussion of the three modifications of carbon, an account of the preparation of many of the more refractory elements and a chapter on carbids, silicids and borids together with a few words on the formation of petroleum. With the appearance of a German edition simultaneously with the issue of the original in French the work becomes equally accessible in both of these languages, and it will doubtless be widely read in both. Both editions are handsomely made up, the margins of the pages, especially, bearing the proper relation to the size of the type, a point which is usually neglected by American publishers. The author has written a special preface for the German edition, outlining in it the work yet to be done with the electric furnace. A complete bibliography of Moissan's papers greatly enhances the value of the book for those who are working in the same field.

To the general public the most interesting part is the chapter on the artificial preparation of diamonds. This work has already been reviewed at some length, this Journal, **1**, 118 (1896), and a reference here will suffice. To the chemist proper the chapter on the compounds of the elements with carbon, silicon and boron will appeal strongly. Barium, calcium, strontium and lithium carbids are attacked by water with formation of acetylene; aluminum and glucinum carbids with formation of methane, while the carbids of yttrium, thorium, cerium and lanthanum give mixtures of these two gases when acted upon by water. The carbid of manganese is decomposed by water with formation of methane and hydrogen, while uranium carbid gives methane, hydrogen and ethylene. Acting with cold water upon this last carbid large quantities of liquid and solid hydrocarbons are formed and the same is true, though to a lesser extent, with cerium and lanthanum. The carbids of molybdenum, tungsten and chromium do not decompose water at ordinary temperatures and chromium enjoys, for the time being, the distinction of being the only element which forms two carbids, the compounds, CCr_4 and C_2Cr_3 having been prepared by Moissan. Titanium, zirconium, vanadium and silicon unite with carbon in the ratio of one to one.

The author makes the very plausible suggestion that some of the natural petroleums are due to the action of water upon metallic carbids formed at a hotter period of the earth's history.

Wilder D. Bancroft

Électro-Metallurgie. *Ad. Minet. 16mo. 195 pages. Gauthier-Villars et Fils; Paris, 1897. Price 2.50, bound 3, francs.* This is a volume of the *Encyclopédie des Aide-Mémoire.* The first part of the book is devoted to the preparation of metals by electrolysis of aqueous salt solutions, with remarks on copper, lead, silver, bismuth and cadmium; on gold, platinum, arsenic and antimony; on iron, nickel, cobalt and zinc. The second part treats of electrometallurgy in the dry way. Under this heading we find electrolysis of metals and electric furnaces. In a book of this size one does not expect to find everything; but that is all the more reason for not taking up valuable space with the following so-called law of Sprague: « In a mixture of several electrolytes, the order of decomposition is determined by the heats of formation of those electrolytes; the substances with the smallest heats of formation will be the first to be decomposed. »

Wilder D. Bancroft

Les Piles Électriques. *Ch. Fabry. 16mo. 170 pages. Gauthier-Villars et Fils; Paris, 1897.* This book is one of the numbers of the *Encyclopédie des Aide-Mémoire* and is intended primarily for engineers. There are chapters on the theory of the cell, on the determination of constants, on the different cells in use and on standard cells. It is all rather rudimentary and there is nothing modern about the treatment. It is a pleasant little book but unsatisfactory to the chemist—for whom indeed it is not intended.

Wilder D. Bancroft

Étude critique du Matérialisme et du Spiritualisme par la Physique expérimentale. *Raoul Pictet. Large octavo, xx and 596 pages. George et Cie; Genève, 1897.* This book was written to show that the mechanical, fatalistic conception of the universe as outlined by Laplace must give way to a nobler view according to which matter acts on matter at a distance without the intervention of a medium while man's freedom of choice is not limited. We start with two experimental entities, ponderable matter and ether, and postulate the attraction of matter for matter and of matter for ether. Everything then becomes intelligible, not to say elementary. Two or more vapor molecules unite to form one liquid molecule and therefore liquids are denser than vapors. Two or more liquid molecules unite to form one solid molecule and therefore solids may be more or less dense than liquids. Nothing could be simpler or less convincing. In books of this character it is impressive to note the way in which difficulties do not occur.

From a brief consideration of the rotation of the earth's axis, of the behavior of compressed gases and of the phenomena of gravitation, the author claims to have found that the kinetic theory of matter is self-contradictory and untenable. Without accepting all the conclusions the reader may well join the author in thinking that a bombardment by particles of ether is an unsatisfactory way of accounting for what we call the force of gravity.

As appendices we have three papers on the theory of gravitation, one on heat and on chemical synthesis. In this last there are some very interesting data on the change of equilibrium with the temperature. The general appearance of the book is marred by the abuse of italics. *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 which bear upon any phase of Physical Chemistry.

General

The Evolution of Physical Theories since the XVII Century. *P. Duhem. Rev. Quest. Sci. (Oct.) 1896.* A very eloquent lecture. After the physics of the schoolmen, made up of comments upon the writings of Aristotle, scholars were led by Galileo to study nature at first hand. The subsequent Cartesian method, in disregarding the qualities of things, led to a belief that nothing exists but matter and motion; after which the Newtonian school concerned itself with observable relations, paying no attention whatever to hypothetical metaphysical or mechanical causes. In the present century the Cartesian mechanistics and the dynamism of Leibnitz are both suffering decline, largely through the influence of thermodynamics. But modern physics is a growth in which the labors of every individual inquirer have played a part. *J. E. T.*

On Necessary and Unnecessary Application of Atomistics in Natural Science. *P. Volkmann. Wied. Ann.* **61**, *196 (1897).* Physical phenomena may be roughly divided into three classes: Coarser phenomena, such as those of elasticity or of capillarity, where the employment of atomistic hypotheses is unnecessary; finer phenomena, such as those of electrolysis or of the dispersion and absorption of light, where atomistic hypotheses may be useful; and a middle field where the usefulness of atomistics may be doubtful. Only in this latter field properly applies Boltzmann's contention (**1**, 434) that the application of both atomistic and phenomenological methods should be developed together. *J. E. T.*

Again on Atomistics. *L. Boltzmann. Wied. Ann.* **61**, *790 (1897).* Boltzmann expresses his agreement with the views of Volkmann—see preceding review—and restates his position, that all concepts of the calculus are of necessity based originally upon ‹atomistic› conceptions,—upon the initial consideration of a finite number of elements. *J. E. T.*

Permanent Changes and Thermodynamics. I: The Permanent Changes of Systems which depend upon a Single Normal Variable. *P. Duhem. Zeit. phys. Chem.* **22**, *545 (1897).* The state of such a system is determined by the thermodynamic temperature T and a variable x (as *e.g.* the volume) so chosen that variation of T alone involves no production of work W, *i.e.* a ‹normal variable›. Then $d'W = Xdx$ when the outer condition X (as *e.g.* $-p$) maintains equilibrium, and we have

$$\varepsilon = \psi - T\cdot\partial\psi/\partial T \qquad \eta = -\partial\psi/\partial T$$

where ε, ψ and η are energy, free energy and entropy ; also the condition of equilibrium

$$X = \partial\psi/\partial x,$$

and for a path,—all these equations relating to a reversible series of states of equilibrium,—

$$dX = \frac{\partial^2\psi}{\partial x^2}dx + \frac{\partial^2\psi}{\partial x\partial T}dT\,.$$

Duhem now considers any possible change, and introduces the fundamental hypothesis that a function ψ always exists such that $\varepsilon = \psi - T\cdot\partial\psi/\partial T$, and that in an irreversible series of equilibria

$$dX = \frac{\partial^2\psi}{\partial x^2}dx + \frac{\partial^2\psi}{\partial x\partial T}dT + f(x,\,T,\,X)\,|dx| \qquad (5)$$

where f is a uniform, finite, continuous function, and $|dx|$ is the absolute value of dx.

In isothermal changes (5) becomes

$$dX = \partial^2\psi/\partial x^2\cdot dx + f\cdot|dx|\,.$$

With rising x, $dx = |dx|$, so

$$dX/dx = \partial^2\psi/\partial x^2 + f,$$

while with falling x, $dx = -|dx|$ and

$$dX/dx = \partial^2\psi/\partial x^2 - f\,.$$

Putting α and β for the tangents to these rising and falling isotherms in the X, x-plane there follows

$$1/\alpha + 1/\beta = 2 \cdot \partial^2\psi/\partial x^2 .$$

Also, assuming dX and dx to have the same sign in all isothermal changes—

$$\partial^2\psi/\partial x^2 > 0 .$$

In isobaric changes dX becomes zero in (5), and so for rising and falling x respectively—

$$\left(\frac{\partial^2\psi}{\partial x^2} + f\right)dx + \frac{\partial^2\psi}{\partial x \partial T}dT = 0$$

$$\left(\frac{\partial^2\psi}{\partial x^2} - f\right)dx + \frac{\partial^2\psi}{\partial x \partial T}dT = 0 .$$

The corresponding absorption of heat λdx is formulated, and, assuming this and dT to have the same sign, there follows

$$\lambda \cdot \partial^2\psi/\partial x \partial T < 0 .$$

The integral of the fundamental equation (5) is

$$X_t - X_0 = (\partial\psi/\partial x)_t - (\partial\psi/\partial x)_0 + \Sigma f\,|dx|$$

whence, for a cycle,

$$\sum f\,|dx| = 0 ,$$

which requires f to change sign,—*i. e.* the path cuts the «natural surface of condition» $f(x, T, X) = 0$ in double points. In infinitesimal cycles, save when starting from this surface, the normal variable is permanently changed by an amount of the order of magnitude of the sum of its absolute changes. The function f, when not in the natural surface, has a sign opposite to that of the permanent change of x; when $\partial f/\partial x > 0$ at the surface the system is termed of the first kind, when $\partial f/\partial x < 0$ it is of the second kind; and it may be shown that under constant T and x the natural surface is stable for the former and instable for the latter. In the natural surface the rising and falling isotherms intersect tangentially, as do also the rising and falling isobars.

When the transition through any continuous series of states in the natural surface is termed a ‹pseudoreversible› process, and

$\int d'Q/T = 0$ is assumed for every pseudoreversible cycle, it is shown that the equations for the entropy and the free energy retain the form which they have in reversible thermodynamics. Assuming $\int d'Q/T > 0$, $d'Q =$ heat evolved, for any realizable cycle, it follows that at constant x, X approaches its value in the natural state. For this state $(\partial X/\partial T)_x$ retains its usual form, as does the analogous expression for $(\partial x/\partial T)_X$. Finally, Clausius's inequality requires that everywhere in the natural surface—

$$1/\alpha - 1/\nu > 0$$

for isothermal cycles (α and ν are dx/dX for the rising isotherm and for the natural isotherm respectively), and

$$\lambda(1/\alpha - 1/\nu) > 0$$

for isobaric cycles, where α and ν relate to the isobars; λdx remains the heat absorbed. *J. E. T.*

Permanent Changes and Thermodynamics. II: The Transformations of Sulfur. *P. Duhem. Mém. sav. étrangers de l'Acad. roy. Belg.* **54** *(1896). Translated, with changes, Zeit. phys. Chem.* **23**, *193 (1897).* This is a very long article, written to demonstrate the value of the author's theory, see above review, through employing it for the complete qualitative description of an important special case—the transformation of ordinary sulfur into the insoluble variety through changes of temperature. The first chapter recapitulates the results of the foregoing paper,—first developing the mathematical treatment with employment of temperature, volume and relative composition x as variables; then transforming it with the replacement of volume by pressure, and of free energy by the thermodynamic potential as the governing potential function; and, finally, formulating it for immediate application under the special condition of constant pressure. In the remainder of the paper this theory is applied in detail to the very complex phenomena, comprehensively studied by Gernez in 1876 and thereafter, of the ‹permanent changes› of liquid sulfur (chapter 2), of monoclinic sulfur (chapter 3) and of the rhombic form (chapter 4). The author considers the influence of the temperature of heating, and of the amount and time of supercooling, upon the final state of liquid sulfur; the influence of the mode of formation, and of the time, during standing or in repeated freezings, in the production of each of the two solid modifications; and, finally, the thermodynamic behavior of sulfur in cycles in which heterogeneous changes of state occur. One is compelled to marvel at the fruitfulness of this theory in supplying a thorough and coherent description of the very complicated relations which here appear. For the mass of detailed applications the reader must be referred to the original paper. *J. E. T.*

Permanent Changes and Thermodynamics. III: General Theory of Permanent Changes. *P. Duhem. Mém. sav. étrangers de l'Acad. roy. Belg.* **54**; *Zeit. phys. Chem.* **23**, *497* (*1897*). Having developed his theory for systems determined by the thermodynamic temperature and one other variable, see (I) above, and in particular for the special case of ‹isopiestic› changes, and having illustrated its bearing through applications to magnetic hysteresis, *etc.* (Mém. Acad. Belg. **54**) and to the transformations of sulfur, see preceding review, Duhem now undertakes to formulate it for systems determined by any number of ‹normal› variables, even when the temperature and the outer conditions are subject to simultaneous variation, and thereby also to bring this theory into connection with his earlier exposition of general thermodynamic theory. He, first, terms a «possible change» a series of equilibria that is the limit of realizable changes, a «purely virtual change» a series that is not such a limit, and he divides ‹possible› changes into reversible ones, where the reverse path is ‹possible›, and irreversible ones, where it is not. He then makes, in general form, the same fundamental assumption as before in regard to the existence of the free energy, of the conditions of equilibrium, and of the equation (5) for a change. There follows hereupon in due order a generalization, for the present case, of the special treatment given in the first paper (see above) of the subtopics of isothermal displacements of equilibrium, of temperature displacements, of cycles, of the «natural state *spaces*» which here replace the former natural state *surfaces*, and of pseudoreversible changes and the apparent entropy and thermodynamic potential which play a part in them. Assumption of the inequality of Clausius leads to the conclusion that every possible irreversible change involves a positive uncompensated transformation, and, further, to the theorem that a natural state is stable when a definite quadratic expression, involving the second derivatives of a potential function, is positive. From this are obtained directly inequalities governing the isothermal displacements and the temperature displacements of the natural states. The paper includes, further, the dynamical equations for the time-rates of permanent changes. The whole investigation is a heavy piece of important work, executed in a clear and rigorous manner; the reviewer can not help adding that the careful German translation, by Bredig, of the three long papers reads wholly like an admirable original. *J. E. T.*

On the Kinetic Theory of Vortex Motion. *L. Natanson. Bull. Acad. Cracovie,* **1897,** *155 (1897).* Deduction of the equations of vortex motion of fluids, starting from the fundamental hypotheses of the kinetic theory. The author thereby sheds light upon the property termed by him «coercion», the action tending to efface disturbances, in establishing that Helmholtz's (1882) and Nanson's (1874) equations of vortex motion are verified when these forces of coercion are required to satisfy the theorem of the moment of momentum.

J. E. T.

On Molecular Forces. *A. Korn. Sitzungsber. Akad. Wiss. München,* **1897,** *181.* A mathematical investigation of the error made by replacing, in d'Alembert's equation, the theoretical density of a continuous medium by the density, of a small volume, actually employed in empirical physics. *J. E. T.*

Reference of Valence to the Action of Attractive and Repulsive Forces and to a Friction in Ether. *F. Rösch. Zeit. phys. Chem.* **23,** *24 (1897).* Mathematical discussion of the behavior of atoms between which are assumed repulsive forces proportional to the third power of the distance. The distance r is determined by

$$m_1 \frac{d^2r}{dt^2} = -\frac{a \cdot m_1 m_2}{r^2} + \frac{c}{r^3} + R ,$$

where R denotes the friction in the ether. The constant of repulsion c is supposed to vary with the temperature and with the motion of light and of electricity. *J. E. T.*

On Scientific and Technical Education. *W. Ostwald. Zeit. Elektrochemie*, **4**, *5* (*1897*). A speech at the fourth meeting of the German electrochemical society in which Ostwald calls attention again to the fact that the present superiority of the Germans in all branches of chemistry is due very largely to the scientific nature of the training at the University. At the meeting there was a violent discussion owing to the desires of some of the members to commit the society to an approval of a law providing for a state examination. Luckily this dangerous and absurd proposal was voted down; but it will be a painful surprise to those foreigners who have studied in Germany to learn that such a proposal could be considered favorably by any University professors. *W. D. B.*

Monovariant Systems

Peculiarities in the Course of the Fusion Curve. *J. D. van der Waals. Kon. Akad. Wetensch. Verslag. Amsterdam.* **1896-97**, *385* (*1897*). From the author's equation for two-component two-phase systems--

$$(V_2 - V_1)dp = W_{21}(d\tau/\tau) + (x_2 - x_1)(\partial^2\zeta/\partial x_1^2)_{p,\tau}\,dx_1$$

W_{21} denoting heat freed upon change of the phase (2) into (1), he finds that the equilibrium temperature is a maximum when the phases have identical composition. The derivative $(\partial^2\zeta/\partial x_1^2)_{p\,\tau}$ between $x = 0$ and $x = 1$ is not infinity, whence follows that $(\partial\tau/\partial x_1)_p = 0$, the curve has a true, rounded maximum. It can not have a break there unless the liquid contains *only* molecules having the composition of the solid—so that adding solvent is adding a foreign body—which looks improbable. This argument is repeated from an earlier publication, in order to controvert the opposed opinion recently advanced by Le Chatelier, Zeit. phys. Chem. **21**, 557, see this Journal **1**, 505. Compare, however, Le Chatelier, Comptes rendus **124**, 1091 (1897). *J. E. T.*

On the Melting Points of Organic Substances. *Franchimont. Kon. Akad. Wetensch. Verslag. Amsterdam*, **1896-97**, *156* (*1896*). After a discussion of the change of melting temperature resulting from the replacement of hydrogen, in organic compounds, by various groups, it is concluded that the resulting change can not in general be foretold—even qualitatively. Approximate rules are, however, valuable, because departures from them lead to further research.

J. E. T.

The Equilibrium of a Compound Solid with Gas and Liquid. *J. D. van der Waals. Kon. Akad. Wetensch. Verslag. Amsterdam*, **1896-97**, *482*; *Arch. néerl.* (*2*) **1**, *78* (*1897*). A study of binary bodies, both of whose components vaporize. The ψ-surface is used, assuming the transverse plait (fold)—that for liquid-vapor—to be present, but not the longitudinal plait—that for liquid-liquid. The ψ-line for the solid lies in a surface parallel with the ψ, V-surface and distant therefrom by an amount x, determined by its composition. Planes tangent to the original surface and to the ψ-line determine what phases can coexist. The first result of the study is (presupposing the gas-laws) the mass law formula of Horstmann for the dissociation equilibrium. Detailed discussion of the surface shows that in a given volume there occurs a maximum temperature for coexistence of solid and vapor (‹maximum sublimation temperature›); then a series of temperatures where solid, liquid and vapor are coexistent, the solid and liquid having identical composition at the highest of them (‹minimum melting temperature›); whereupon follows coexistence of solid and liquid under increased pressures. If the solid have a greater volume than the liquid, the system may reach the highest temperature at which the three states can coexist; in this event the composition of the solid will lie between the compositions of the liquid and of the vapor (‹maximum melting temperature›). The most of these conclusions can be drawn from earlier formulas representing the dependence of pressure upon temperature for three-phase systems, «for which the researches of Roozeboom have furnished so ample a series of applications». *J. E. T.*

Fusion Lines for Systems of Two and Three Organic Substances. *H. W. B. Roozeboom. Kon. Akad. Wetensch. Verslag. Amsterdam*, **1897-98**, *62*. **Application of the Phase Rule for the Investigation of Organic Addition Products.** *B. Kuriloff. Zeit. phys. Chem.* **23**, *547* (*1897*). The Dutch paper gives the temperature-composition diagrams for two-component monovariant systems, where : 1, no stable compound is formed, and the two fusion curves intersect ; 2, one solid compound appears, and has a stable melting point ; 3, the solid compound has an instable melting point. It adds a report of Kuriloff's work, in which the second type was realized with naphthol and picric acid, benzene and trimethylmethane, and benzene with trinitrobenzene. The observations confirmed the general principle that the curve for the compound has its shorter branch on the side of the less volatile component. Benzene with picric acid illustrates the third type ; here the transition point nearly coincides with the instable melting point. With the ternary system : benzene, picric acid and naphthol, two two-branch isotherms were determined for the compound of the last pair, in equilibrium with liquid and vapor. The details of the investigation with benzene and triphenylmethane are given in Kuriloff's paper ; the compound melts at 78.2° and its solubility curve cuts the curve for triphenylmethane at 74°. Triphenylmethane gives normal freezing temperature depressions in benzene (to within 4 pct). *J. E. T.*

The Contraction of Certain Organic Compounds on Freezing. *A. Heydweiller. Wied. Ann.* **61**, *527* (*1897*). Very exact dilatometric determinations of the specific volumes of six compounds above and below their melting temperatures, together with determination of the extent of the metastable state in each case. The data are presented in tables and curves. The change of volume on fusion could not be brought into relation with any other physical quantity, though the attempt was made to equate the decrease (during freezing) of the potential energy—

$$\int_{v_s}^{v_f} \frac{a}{v^2}\, dv = a\left(\frac{1}{v_s} - \frac{1}{v_f}\right) = a(s_s - s_f)$$

with the heat of fusion. The two values of *s* denote the specific gravities of solid and of liquid. The value of *a* so found for benzene was five times the value $a = 3p_k v_k^2$ calculated from the critical data, from which is concluded that during freezing the inner pressure increases much more rapidly than is indicated by the van der Waals equation,—a conclusion which is strengthened by the great concomitant increase of viscosity. *J. E. T.*

The Heats of Vaporization of Liquids. *S. R. Milner. Phil. Mag.* [*5*] 43, *464* (*1897*). Previously cited measurements (1, 582), of the heats of vaporization of benzene, extended to 50° instead of 40°; and certain energy equations (1, 623) were expressed in heat units instead of in work units. *J. E. T.*

Addition to my Paper: On Saturated Solutions of Magnesium Chlorid and Potassium Sulfate or of Magnesium Sulfate and Potassium Chlorid. *R. Löwenherz. Zeit. phys· Chem.* 23, *95* (*1897*). In the earlier paper it was not stated that the values for the concentration of the solution in equilibrium with KCl, $MgKCl_3 6H_2O$ and $MgSO_4 6H_2O$ were very different when the solution had not been heated above 25° and when it had been. *W. D. B.*

On the Decomposition of Seignette Salt and of the Corresponding Ammonium Compound. *J. D. van Leeuwen. Zeit. phys. Chem.* 23, *33* (*1897*). At 55° there is a quintuple point with Seignette salt, dextro sodium tartrate and laevo sodium tartrate as solid phases, the reaction being:

$$2NaKC_4H_4O_6 4H_2O - 5\tfrac{1}{2}H_2O \rightleftarrows Na_2C_4H_4O_6 2H_2O$$
$$+ K_2C_4H_4O_6 \tfrac{1}{2}H_2O$$

The double salt is decomposed by water with precipitation of sodium tartrate above 40°. At 59° there is a corresponding point for the system, dextro sodium tartrate, dextro ammonium tartrate and water:

$$2NaNH_4C_4H_4O_6 4H_2O - 6H_2O \leftrightarrows Na_2C_4H_4O_6 2H_2O + (NH_4)_2C_4H_4O_6$$

From the change of vapor pressure with the temperature, the author finds 2500 cal. for the heat of reaction with Seignette salt while Berthelot's measurements of the heats of solution reduce to 2373 cal. *W. D. B.*

On the Maximum Depression of the Freezing Point of Mixtures. *E. Paternò and G. Ampola. Gazz. chim. Ital.* 27, *I, 481* (*1897*). A collection of valuable preliminary determinations of freezing point curves for binary systems. In some cases determinations were made at temperatures below the eutectic temperature. These are probably observations on supersaturated solutions. A great deal of space is wasted in discussing the obsolete question whether eutectic mixtures are compounds or not. *W. D. B.*

On Cryohydrates. *G. Bruni. Gazz. chim. Ital.* **27**, *I, 537 (1897)*. This paper is chiefly a rehash of other people's work and is a mass of errors. The good points are a determination of the cryohydric curve for magnesium and zinc sulfates in aqueous solution and a revision of Mazotto's figures. *W. D. B.*

Experimental Studies of Gas Hydrates. *P. Villard. Ann. Chim. Phys. (7)* **11**, *289 (1897)*. Nitrogen monoxid, carbon dioxid, sulfur dioxid, acetylene, ethylene and methyl chlorid all crystallize with six of water and the author generalizes from this that all gases crystallize with six of water in cubical cystals. In order that there shall be no exceptions to this rule, the haloid acids are not classed as gases. Roozeboom found seven of water in the sulfur dioxid compound; but Villard does not accept this. The system, nitrogen monoxid and water, has been studied somewhat in detail, the others only superficially. The author proposes the following incorrect law: «The hydrate has the same dissociation pressure in the solution as in presence of the vapor». The mistake here is the assumption that the hydrate has a definite dissociation pressure when no solution is present.

Ethyl chlorid, methyl iodid, methylene chlorid, chloroform, ethylidene chlorid, chlorethylene, ethylene chlorid, ethyl iodid, ethyl bromid, carbon terachlorid and carbon bisulfid all form compounds with water, which were not analyzed. Of great interest are the author's experiments upon the effect of a so-called indifferent gas upon the stability of gas hydrates. The indifferent gases increase the pressure of the system and exert a solvent action upon the components. *W. D. B.*

Complete Freezing-point Curves of Binary Alloys containing Silver or Copper together with Another Metal. *C. T. Heycock and F. H. Neville. Phil. Trans.* **189** *(A) 25 (1897)*. Silver and copper give a normal curve from a qualitative point of view. With silver and lead or silver and tin there is a curious waviness in the branch along which silver is solid phase. Copper and lead form two liquid layers, as do copper and bismuth. In the copper-tin curve there are two quadruple points in addition to that at the eutectic temperature. It is not certain what the solid phases are; but it is safe to assume that some are solid solutions. With silver and antimony there is a distinct break in the curve at twenty-five «atomic percents» of antimony. The curve for silver and bismuth is said to have a similar break. The systems, gold and copper, silver and thallium, were not studied in detail.

Addition of gold or platinum to silver raises the freezing-point. The same phenomenon occurs when nickel or iron is added to copper. With iron and copper the freezing point soon ceases to rise as if the metals were only partially miscible and a solid solution formed the fourth phase at the quadruple point. For a preliminary reference to this paper, see this Journal, **1**, 312 (1897). *W. D. B.*

Divariant Systems

On the Question whether the Molecular State of a Solvent Influences the Lowering of Pressure which Dissolved Salts effect. *J. D. van der Waals. Kon. Akad. Wetensch. Verslag. Amsterdam,* **1896-97,** *342 (1897)* The author's molecular theory of two-component systems, assuming both components to consist of unchanging molecules, gives for the equilibrium pressures at high dilutions the usual relation $-d\log p/dn = 1/(N+n)$, a relative decrease of vapor pressure which becomes twice as much if a molecular weight of the solute can form two of ions. Smits found the values of this factor to pass a maximum less than 2, so van der Waals examines what change must occur in his ψ-surface (and, from this, in the vapor pressures of dilute solutions) when x molecules of solute and $1-x$ of solvent yield $2y$ ions and z double molecules—a total of $1+y-z$. Calculation of the case leads to $-d\log p/dx = 2$ for indefinitely dilute solutions. It can be shown, however, in any event, that the limiting value of this factor must be identical with that obtained from the observed freezing temperatures. To study equilibria involving a solid phase one must consider rolling planes tangent simultaneously to the ψ-surface and to the «ψ-line» which in it represents the solid. *J. E. T.*

The Connection between the Laws of Boyle, Gay-Lussac, Joule, etc. *G. Bakker. Zeit. phys. Chem.* **22**, *543* (*1897*). Bakker had shown, Ibid **17**, 684, that each of the five simple gas-laws (see **1**, 198) involves the remaining four if it be assumed that $p(v-b)=RT$ holds for high temperatures and low densities. Overlooking this assumption, Baynes asserted, Ibid **18**, 355, that the result reached requires the assumption of a sixth law ; to which Bakker replies (**1**, 198) that his assumption suffices for the purpose. Baynes then shows (**1**, 442) that all five laws are immediate consequences of the assumed equation of condition ; to which Bakker now retorts that this equation is *not* assumed, save as a limiting value for the special conditions of high temperatures and low densities. It then follows that, for every temperature and volume,—

$$p=\frac{RT}{v-b}-T\int_{T}^{\infty}\frac{1}{T^2}\left(\frac{d\varepsilon}{dv}\right)_{T}dT$$

and
$$v-b=\frac{RT}{p}+T\int_{0}^{\infty}\frac{1}{T^2}\left(\frac{d\chi_1}{dp}\right)_{T}dT,$$

where $\chi_1=\varepsilon+p(v-b)$, and herefrom that each simple law involves the remaining four.

J. E. T.

Papers, from the University Laboratory of Physics at Leiden, on the Applications of van der Waals's Theory of Fluids.

1. *The Critical State, and the ψ-surface for Two-component Systems.* Upon heating Natterer tubes to the critical temperature the separating surface has been observed to disappear at different temperatures, whence various observers have concluded that the Andrews-van der Waals view of the critical state is incorrect. Gouy had ascribed the phenomenon to the influence of gravity, and J. P. Kuenen—On the abnormal phenomena near the critical point, *Verslagen der Koninklijke Akademie van Wetenschappen te Amsterdam*[1], **1893-94**, 85 ; *Communications from the Laboratory of Physics at Leiden*[2], no. *8*, 9—now shows independently that the variations

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[1] To be hereinafter denoted by *V.*

[2] To be hereinafter denoted by *C.*

from theory vanish when the substance is well stirred (with an electromagnetic stirrer). He shows further that the evaporation or condensation is retarded by the presence of impurities, depending upon whether these are chiefly in the liquid or in the vapor phase. Galitzine, in later experiments, found great differences of density between ether on one side of a U-tube and ether with its vapor on the other, when the two masses were separated by mercury and the temperatures lay above the critical. Kuenen hereupon—Some experiments regarding the anomalous phenomena near the critical point, *V.* **1894-95**, 19 and 57 ; *C.* *11*, 1 and 24—shows this result to have been due to the presence of gaseous impurity, probably air. These discussions and experiments are followed by a very instructive paper by Kuenen—On the influence of gravitation on the critical phenomena of simple substances and of mixtures, *V.* **1895-96**, 41 ; *C.* *17*, 1—where this extremely interesting subject is carefully developed for one-component and two-component systems. Compare the recent publications of Villard.

Another series of researches by Kuenen relates to the vaporization phenomena of binary mixtures. In his dissertation—Measurements concerning the surface of van der Waals for mixtures of carbonic acid and methyl chloride ; Leiden, 1892 ; abstracted in *V.* **1891-92**, 422 ; abstract translated in *C.* *4*, 1 ; paper expanded in *Arch. néerl.* (1) **26**, 354 ; fully abstracted in *Zeit. phys. Chem.* **11**, 38 (1893)—Kuenen undertakes to determine isothermals for three mixtures of CO_2 and CH_3Cl between 25° and 160°, in order to calculate the constants of Clausius's equation and with them to construct the volume-composition-free energy surface (the v, x, ψ-surface) studied by van der Waals—*Arch. néerl.* **24**, 1 ; *Zeit. phys. Chem.* **5**, 133 (1890). He showed that the critical temperatures do not agree with Pawlewski's law, and he tabulated the variations from Dalton's law and the increase of pressure on mixing at constant volume. In the continuation of this work—On retrograde condensation and the critical phenomena of mixtures of two substances, *V.* **1892-93**, *15* ; *C.* *4*, 7—he points out that, according to the Waalsian theory, these binary mixtures fall into three groups,—those where a separation into two coexisting phases is impossible, those where the lighter phase is continuously condensed upon the heavier with rising pressure, and those where ‹retrograde condensation› occurs. The last case is then realized with a mixture containing 41 pct of CO_2. In another paper—Some experiments about the connection between the two plaits in the surface of van der Waals for mixtures, *V.* **1893-94**, 28; C. *7*, 1—Kuenen discusses the form of the surface for the case where two liquid phases can appear, and fruitlessly seeks realization of it with mixtures of CH_3Cl and CO_2, of CO_2 and air (which is not a two-component system), and of CO_2 and CS_2. The next publication—On the condensation of a mixture of two gases, *V.* **1894-95**, 90; *C. 13*, 1—is a criticism of Duhem's chapter on the same subject in the third memoir of this author's *Dissolutions et Mélanges*. Duhem had concluded that for two groups of mixtures, contiguous to the two components, condensation below the critical temperature must be normal, while for the intermediate groups it *may* be retrograde. Following the Waalsian theory, Kuenen shows that the condensation *must* be retrograde between two definite temperatures for *all* possible mixtures, and he upholds his priority in the prediction as well as in the experimental confirmation of the phenomenon. He then, following Duhem's method, develops the complete theory in detail and illustrates it by a diagram, drawn to scale, for mixtures of CO_2 and CH_3Cl, and he repeats (from the paper in *Arch. néerl.* **26**) the prediction that a second kind of retrograde condensation is possible, where compression will cause the appearance and the subsequent disappearance of a phase of vapor. Compare Duhem's later paper in this Journal, **1**, 273. In the final publication of this series—On the condensation and the critical phenomena of mixtures of ethane and nitrous oxide, *Phil. Mag.* **40**, 173 (1895); revised in *C. 16*, 1; reprinted in *Arch. néerl.* (2) **1**, 24 (1897)—Kuenen shows that, considering the x,v-projection of the ψ-surface and supposing no two liquid layer plait to interfere, two general cases are to be distinguished; either the plaitpoint lies nearer the x-axis than does the critical point of contact, or the contrary is true. In the first case the condensation between the temperatures of these points is retrograde of the first kind, in the second it is retrograde of the second kind. Representation in the p,t-plane will show: 1, The two vapor pressure curves of the components; 2, The two-branch «border curves» for all successive two-phase mixtures; 3, The plaitpoint curve, connecting the critical points of the components and supplying the envelope of the border curves. Experiments with C_2H_4 and N_2O failed to show the retrograde condensation of the second kind, but they did exhibit some mixtures with critical points lying below those for the components, and some with critical points lying outside the region between the two vapor pressure curves, so that the plaitpoint curve midway in its course cuts the higher vapor pressure curve. Exhaustive discussion of the peculiarities of this case conclude the paper.

2. *Low Temperatures.* In an early investigation, published by the Amsterdam Academy in 1881 and recently reprinted—General theory of the fluid state, *Verhand. Amst. Akad.* **21**, (1881); *Arch. néerl.* **30**, 101 (1896)—H. K. Onnes, the present head of the Leiden laboratory, was concerned with developing the isotherms of fluids, by employing the kinetic theory with especial assumption of the similarity of molecules and of their motions. From simple assumptions, and abandoning the constancy of the b of van der Waals's equation, he finds

$$R(1+\alpha t) = (p + a/v^2)(v - rm)\cdot\chi(m/v),$$

m being the total volume occupied by the molecules, r the ratio b/m for all substances, and χ a function of the collisions. From this isotherm he then derives the critical data and the reduced form of the isotherm. He deduces then, in another way, from his fundamental principle of similarity, that the ratios of corresponding pressures, volumes and temperatures are those of the critical values of these variables, and in a similar line of argument he concludes that the reduced vapor pressure curve is the same for all substances. The equation which he finds is, for $\chi = 1$, identical with that of van der Waals. Part II of the paper elaborates the idea that, for different substances, the similarity of the isotherms is the expression of the similarity of the molecular motions, and from the principle he derives the further results that the capillarity constants, the coefficients of viscosity and the coefficients of heat-conductivity of two liquids in corresponding states stand in constant ratios, which are expressible in terms of the molecular constants.

Onnes's studies of the law of corresponding states indicated the desirability of investigating the dependence of the Waalsian a and b upon volume and temperature, for which purpose substances with widely separated critical temperatures should be examined, and whereby also disturbances due to chemical changes and to the mobility of the parts of molecules would be expected to be minimized. This led him to the development of a ‹cryogenic laboratory›—On the cryogenic laboratory at Leiden and on the production of very low temperatures, *V.* **1894-95**, 164; *C. 14*, 1—where physical experiments could be conducted in liquid baths at low temperatures, and where in particular the isotherms of the more permanent gases, especially hydrogen, could be studied. The installation comprises three cycles, one of methyl chlorid for temperatures from − 23° to − 70°, one of ethylene reaching from − 103° to − 140°, and one of oxygen for temperatures below − 182°. The apparatus for each cycle forms a closed whole, to avoid waste of material, and the three can be connected into a continuously working cascade for the production of baths of liquid oxygen. Onnes hopes eventually to decant liquid hydrogen—Remarks on the liquefaction of hydrogen, on thermodynamical similarity and on the use of vacuum vessels, *V.* **1895-96**; *C. 23*, 1;—in discussing the problem he considers how the necessary constructions may be deduced from the action of a model working with oxygen, using for this his theorem (see *théorie générale* above) that in corresponding states the molecular motions of all substances are dynamically similar. The rest of the paper treats Linde's method, the work of Dewar and the construction of vacuum receptacles. A curious feature of this subject is a report by the Amsterdam Academy—Report of the commission on the danger of the presence of compressed gases in the physical laboratory at Leiden, *V.* **1896-97**, 3—to the Dutch government, concerning formal complaints that dangerous explosions might occur in the new cryogenic laboratory. After due examination, and correspondence with the heads of similar laboratories—Dewar, Olszewski, Pictet, *etc.*,—it was reported that such fears were ill-founded. There remain for mention Onnes's completed thermometric appliances—On the measurement of very low temperatures, I and II, *V.* **1896-97**, 37 and 79—these consisting of a constant-volume hydrogen thermometer and of a copper-German silver thermoelement. *J. E. T.*

On the Complete Calorimetric Study of a Salt. *E. Monnet. Thèse, Bordeaux, 1897.* Determinations of the heats of solution and of hydration of both hydrated and anhydrous sodium acetate, together with the heats of dilution of the (aqueous) solutions and the specific heats of the solid salts and of their solutions. The tabulated results are expressed analytically and represented by curves.

J. E. T.

On the Influence of Water on the Solubility of Some Compounds in Ether. *H. Schiff. Zeit. phys. Chem.* **23**, *355 (1897).* Phloretin is much more soluble in aqueous ether than in ether or water alone. The data were originally published in Liebig's Annalen, **229**, 371 (1885). *W. D. B.*

A Study of Ferric Hydroxide in Precipitation. *V. J. Hall. Am. Chem. Jour.* **19**, *512 (1897).* If we add less than the theoretical amount of caustic potash necessary for precipitation to a solution of ferric sulfate, this latter salt is occluded; otherwise potassium hydroxid is carried down. There is a strong suggestion of quantitative relations; but the experiments are by no means conclusive in respect to this point. When ferric chlorid is used, less iron salt is occluded. The reviewer regrets the appearance of the phrase «mechanical inclusion». *W. D. B.*

Velocities

On Irreversible Processes, I. *O. Wiedeburg. Wied. Ann.* **61**, *705 (1897).* It is desirable to extend the thermodynamics of reversible processes, which describe only equilibria, to actual processes which occur with finite velocities. We now employ a special elementary law for each kind of phenomenon, but the similarity of these laws incites us to seek a uniform formal description of all velocities; such a formulation the author presents in the present paper. He recalls that for the inner energy E in reversible changes

$$dE = \Sigma l dM, \qquad \text{(III)}$$

where the M's are characteristic quantity-coordinates, as entropy, volume, electrical quantity, *etc.*; from which equation are derivable «thermodynamic relations» of the form

$$\partial I / \partial M' = \partial I' / \partial M. \qquad (7)$$

These relations of symmetry lead him to write the n equations of condition relating the $2n$ variables M and I, in the form

$$\left.\begin{aligned} dI &= \mu dm + \lambda dM' \\ dI' &= \mu' dM' + \lambda dM. \end{aligned}\right\} \qquad (8)$$

He then considers any reversible or irreversible changes, and first postulates a conservation law—

$$dM_1 + dM_2 = 0\,,$$

which shall hold even for the entropy. The time-rates of transfer between two bodies are then

$$\frac{dM_1}{dt} = -\frac{dM_2}{dt} \qquad (10)$$

and the author writes for the energy taken up by a body (i) in unit time

$$\eta_i = I_i \frac{dM_i}{dt} + W_i \left(\frac{dM_i}{dt}\right)^2 \qquad (11)$$

whence, by (10), for both bodies

$$\left(W_1 + W_2 \right) \frac{dM_1}{dt} = I_2 - I_1 \qquad (13)$$

the familiar velocity equation, the author's «intensity law»; equation (11) is evidently chosen to correspond with this result. W is a generalized resistance, the name indicating that with given $I_2 - I_1$ the velocity falls as $W_1 + W_2$ rises. From $\eta = \eta_1 = -\eta_2$, and (10) we get

$$\eta = I_2 \frac{dM_1}{dt} - W_2 \left(\frac{dM_1}{dt}\right)^2, \qquad (14)$$

which shows that the energy taken up in a change of M_1 depends upon the parameters which determine the W_2 of the other body. For heat conduction, (13) and (14) become

$$dS_1 = \frac{\theta_2 - \theta_1}{W_1 + W_2}\, dt \qquad (16)$$

$$d'Q = \theta_2 dS_1 - W_2 (dS_1/dt)^2 dt, \qquad (17)$$

of which (16) is really Fourier's equation, and (17) contains Clausius's inequality

$$d'Q < \theta_2 dS_1 \ ;$$

(17) is given as the complete expression of the second law.

Just as $de = IdM$, for reversible processes, is generalized [equation (11)] by adding a quadratic term, so are the equations of condition (8) for reversible changes, generalized—

$$dI = \mu dM + \lambda\, dM' + \ldots$$

becoming

$$cdI = \quad dM \quad + \quad gdM' \quad + \ldots$$
$$- \kappa \left(\frac{dM}{dt}\right)^2 dt + \gamma \left(\frac{dM'}{dt}\right)^2 dt + \ldots$$

where, to simplify the physical interpretation, the (probably constant) factors are so chosen that the coefficient of dM is unity and the sign of $(dM/dt)^2$ is negative. The equation asserts the change of every intensity to depend both upon the change and the velocity of the change; it is illustrated by application to the torsion of a cylinder.

The author thinks it unfortunate that in the historical development of heat theory the idea of thermal quantity was not reserved for the quantity-coordinate, the entropy. An important outstanding problem is the dependence of the ‹ resistences › upon the factors of the above equations of condition. *J. E. T.*

Velocity of Urea Formation in Aqueous Alcohol. *J. Walker and S. A. Kay. Jour. Chem. Soc.* **71**, *489 (1897).* By making simultaneous determinations of the chemical composition and electrical conductivity of the solutions, the authors were able to use the change in the latter as a means of measuring the change in the former. The addition of ethyl alcohol increases the reaction velocity, though decreasing the dissociation. Methyl alcohol, acetone, glycol, glycerol and cane sugar increase the reaction velocity. The reviewer would suggest that the question of the influence of the solvent on the reaction velocity would probably be simplified if we were to take into account the relative solubilities of the reacting subtances in the solvent. It seems almost certain that the reaction velocity will be higher if the original substances are sparingly soluble in the solvent and the decomposition products very soluble. Of course, in general, the case will not be as simple as this; but it is by work along this line that the problem will be solved.

For any given mixture of alcohol and water a good constant was obtained when the reverse transformation of urea into cyanate was taken into account as well as the change in the dissociation of the cyanate. *W. D. B.*

On the Influence of Pressure on Reaction Velocity in Homogeneous Liquid Systems. *A. Bogojawlensky and G. Tammann. Zeit. phys. Chem.* **23**, *13* (*1897*). In order to show that the effect of pressure is less with a strong acid than with a weak acid, the authors studied the catalysis of methyl acetate by hydrochloric acid and acetic acid. An increase of pressure of five hundred atmospheres increased the constant some twenty percent in the first case and about thirty-seven percent in the second case. With methyl acetate and ammonia the same increase of pressure increased the constant forty to ninety percent, depending on the concentration. The theoretical treatment is marred by the assumption that the active mass of a non-electrolyte is but a small fraction of its total mass. *W. D. B.*

Explosion of Chlorine Peroxide with Carbonic Oxide. *H. B. Dixon and E. J. Russell. Jour. Chem. Soc.* **71**, *605* (*1897*). When a dried mixture of chlorin peroxid and carbonic oxid is made to explode the carbonic oxid is not burned completely to carbon dioxid. From this the authors conclude that nascent oxygen is not perceptibly more active than oxygen gas. *W. D. B.*

An Attempt to cause Helium or Argon to pass through Red-hot Palladium, Platinum or Iron. *W. Ramsay and M. W. Travers. Chem. News.* **75**, *253*; *Proc. Roy. Soc.* (*1897*). No transpiration could be observed at the temperature of the blow pipe, 900° or 950°C. *J. E. T.*

Electromotive Forces

On the Measurement of Polarization Capacities. *C. M. Gordon. Wied. Ann.* **61**, *1*, (*1897*). The method has already been referred to, this Journal **1**, 323 (1897). It is suitable only for low current densities. The capacity is independent of the period for oscillations of 5000–10000 per second. The capacity of mercury electrodes was found to vary nearly proportionally to the concentration of mercury as ion. With platinum electrodes the capacity is a function of the occluded hydrogen or oxygen as well as of the concentration of the electrolyte. To many the most interesting feature of the paper will be the respectful recognition of Warburg's theories upon potential differences. *W. D. B.*

Reply to Nernst. *A. H. Bucherer. Elektrochem. Zeit.* **4**, *70 (1897)*. In considering a particular reversible cycle Bucherer omitted all reference to the heat of vaporization of zinc, because Ostwald's treatment of the relation between heat of ionization and change of electrolytic solution pressure with the temperature leads to results not in accordance with the fundamental principles of thermodynamics. This letter tries to show the fallacy in Ostwald's treatment; but ignores entirely the main question, why Bucherer should make mistakes deliberately because he thinks Ostwald has made one unconsciously. The difficulty in the Ostwald–Bucherer discussion seems to be the assumption that heat is evolved when zinc passes from the state of metal into that of ion. *W. D. B.*

Electrolysis and Electrolytic Dissociation

Remark upon a Paper by Messrs Stroud and Henderson. *F. Neesen. Verh. phys. Ges. Berlin*, **16**, *141 (1897)*. The method of Stroud and Henderson, for measuring electrolytic resistances with constant currents, this Journal **1**, 450, is identical with that described by Neesen in Wied. Ann. **23**, 482 (1884). *J. E. T.*

On the Internal Resistance of Voltaic Cells. *E. Haagn. Zeit. phys. Chem.* **23**, *97 (1897)*. The method consists in placing two condensers of known capacities in the Wheatstone's bridge, a known and variable resistance forming the third side while the cell to be studied occupies the fourth side. For cells with low polarization capacity, Gordon's method, this Journal **1**, 323 (1897), should be employed. Measurements with various cells showed that the internal resistance varies but slightly with the amount of current passing. This is in flat contradiction with Streintz's measurements, which latter are unquestionably wrong. The internal resistances of several accumulators were also determined, both when being charged and discharged. *W. D. B.*

Physical-chemical Basis and Employment of Cataphoresis in Medicine. *R. Mewes. Elektrochem. Zeit.* **4**, *49* (*1897*). By cataphoresis is meant the transfer of the solution by the electric current as opposed to the migration of the ions. There is no justification for the assumption that, by cataphoresis, substances can be carried through diaphragms which they can not pass by diffusion. This particular paper is merely a brief sketch of a book on cataphoresis by Max Aker-Blom of Finland. *W. D. B.*

Contribution to the Study of the Electrical Resistance of Solutions as a Function of Pressure and Temperature. *S. Lussana. Nuovo Cimento,* (*4*) **5**, *357* (*1897*). The change of the logarithm of the resistance with the change of temperature increases with increasing dilution tending toward the same limiting value for all electrolytes as was first stated by Kohlrausch. The limiting value decreases with rising temperature. At constant temperature increase of pressure decreases the resistance as had previously been found by Fanjung. The author's measurements cover a range of one thousand atmospheres pressure. *W. D. B.*

On the Preparation of Thallium by Electrolysis. *F. Foerster. Zeit. anorg. Chem.* **15**, *71* (*1897*). The author electrolyses thallium sulfate between platinum and copper electrodes with a current density at the cathode of 1.3–1.5 amperes per square decimeter and a potential difference of about 3.5 volts. *W. D. B.*

Contribution to the Quantitative Electrolysis of the Heavy Metals. *L. Wolman. Zeit. Elektrochemie,* **3**, *537* (*1897*). Tables showing the results obtained by electrolytic precipitation of silver, copper, lead, manganese, zinc, cobalt and nickel; also analytical data for the separation of copper from nickel or zinc or from both these metals; for the separation of cadmium from zinc; of lead from zinc, silver or copper, and of silver from copper. *W. D. B.*

Quantitative Determination of Nitric Acid by Electrolysis. *K. Ulsch. Zeit. Elektrochemie,* **3**, *546* (*1897*). The cathode is a large spiral of copper wire which is heated in the gas flame to a dull red and then plunged into cold water. The anode is platinum. To the solution of nitric acid or a nitrate sulfuric acid is added and electrolysis is carried on with 4 volts and current density = 1.47. No hydrogen is evolved until about ninety percent of the nitrate has been carried over into ammonia. Some ten minutes after the hydrogen begins to appear, the reduction is complete. An excess of sulfuric acid and the absence of chlorids are two essential features. *W. D. B.*

Structure Phenomena

The Emissivity of Certain Metals for Röntgen Rays. *W. Kaufman. Verh. phys. Ges. Berlin,* **16**, *116* (*1897*). The determinations were made by exposing photographic plates to x-light reflected from polished metal surfaces. Rising emissivity was found in the order Al, Fe, [Ni, Cu, Sn, Zn], Ag, [Cd, Pt, Pb, U], the order in the brackets remaining uncertain. The order is not that of the combining weights; it could not be compared with that of the absorptivity for lack of sufficient data with regard to the latter. The rays are absorbed by a given metal to the same degree no matter from what metal they are emitted. *J. E. T.*

Permeability to X-Rays. *J. Waddell. Chem. News,* **75**, *263* (*1897*). All elements whose combining weights are less than 30 are more permeable than those whose combining weights are above 40; the intermediate elements «fill the transition space imperfectly». *J. E. T.*

The Chemical Action of Light. *J. Gibson. Zeit. phys. Chem.* **23**, *349* (*1897*). The author cites instances to show that the action of light always produces a change to a system which conducts electricity better than the initial one. *W. D. B.*

Yellow Light for the Polariscope. *F. Dupont. Bull. Soc. Chim. Paris,* **17**, *584* (*1897*). Sodium chlorid and tribasic sodium phosphate, melted together in nearly molecular proportions, melt more readily than sodium chlorid, the mixture does not decrepitate and it gives a remarkably steady and brilliant light. For observations with the polariscope it is immensely superior to common salt. *J. E. T.*

On the Change with the Temperature of the Coefficients of Elasticity of Various Glasses. *A. Winkelmann. Wied. Ann.* **61**, *105* (*1897*). Presence of sodium and potassium increase the temperature-coefficient while boric acid decreases it. No quantitative relations could be found. *W. D. B.*

Experiments on Fluid Viscosity. *A. Mallock. Phil. Trans.* **187** (**A**), *41* (*1896*). Measurements of the moment transmitted, by fluid viscosity, across the annular space between two concentric cylinders, one of which revolves while the other is stationary. *W. D. B.*

Surface Tension of Salt Solutions. *H. Sentis. Jour. de Phys.* (*3*) **6**, *183* (*1897*). If F is the surface tension of the salt solution; f that of water at the same temperature; n the volume of 100 reacting weights of water; v that of the mixture of $100 - n$ reacting weights of water and n reacting weights of anhydrous salt, the author finds the relation:

$$F\sqrt[3]{\frac{v}{n}} = \frac{100-n}{100}f + \Phi$$

where Φ is independent of the temperature, between 0° and 30°, and Φ/n is practically constant for salts which crystallize in the anhydrous form. From other experiments the author concludes that the contact angle with water is zero when the walls are thoroughly wetted but that this is not so if the wall be allowed to dry. *W. D. B.*

Papers, from the University Laboratory of Physics at Leiden, on Capillarity. Because of the prominent part played by capillarity in van der Waals's theory of fluids a considerable attention has been given to this subject in Onnes's laboratory. L. M. J. Stoel—Measurements on the influence of temperature on the viscosity of fluids between the boiling-point and the critical state, Dissertation, Leiden, 1891; *V.*[1] **1891**, (Feb.); *Physik. Revue*, **1**, 513 (1892); *C.*[2] *2*, 1—early supplied the hitherto lacking measurements between boiling temperature and the critical point, finding for methyl chlorid that the times

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[1] *V* denotes Kon. Akad. Wetensch. Verslagen, Amsterdam; see p. 688.

[2] *C* denotes Comm. Lab. Phys. Leiden; see p. 688.

of transpiration in tubes satisfy the relation $\mu p^{1/3} = const.$, where μ = coefficient of viscosity under the vapor pressure p. This was followed by work in which E. C. de Vries—Measurements on the influence of temperature on the capillary elevation of ether between the critical state and the boiling point of ethylene, Dissertation, Leiden, 1893; *V.* **1892-93** (Feb.); *C. 6*, 1; *Arch. néerl.* **28**, 210—measured the capillarity of ether from — 100° to the critical point, finding the capillary rise to be a linear function of the temperature. The observed surface energy does not agree with the formula of Eötvös. In subsequent work by M. de Haas—Measurements concerning the coefficient of viscosity of methyl chloride in absolute measure between the boiling-point and the critical state, Dissertation, Leiden, 1894; *V.* **1893-94**, 123; *C. 12*, 1—Stoel's relative numbers for the coefficient of viscosity were replaced by absolute values. Compare the work of Heydweiller. These results enabled Onnes—The coefficient of viscosity for fluids in corresponding states, *V.* **1893-94**, 126; *C. 12*, 9—to test, near the critical temperature, his relation[1] between the coefficients of viscosity of two liquids, here CH_3Cl and CO_2, at corresponding temperatures. A satisfactory agreement was found. A subsequent note—On the coefficient of viscosity of liquids in corresponding states according to calculations of Dr. M. de Haas, *V.* **1894-95**, 62; *C. 12*, 12—contains this comparison for over fifty organic compounds, whose coefficients of viscosity had been calculated by de Haas; the agreement is good for the aliphatic esters, but bad for their alcohols and acids. About this time van der Waals worked out his thermodynamic theory of capillarity—Thermodynamic theory of capillarity under the assumption of continuous changes of density, *Verhand. Amst. Akad.; Arch. Néerl.* **28**, 121; *Zeit. phys. Chem.* **13**, *657* (*1894*). His results furnished the starting point for J. Verschaffelt's measurements—Measurements concerning the capillary ascension of liquefied gases, *V.* **1895-96** (June); *C. 18*, 1—with CO_2 and N_2O. The surface energy σ could be represented by van der Waals's equation

$$\sigma = A(1 - m)^B$$

where m is the reduced temperature and A and B are constants in-

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[1] See page 691.

dependent of the nature of the liquid. A and B were shown to hold constant for five other liquids also. According to the theory the temperature derivative of the surface energy should remain the same function of the temperature; at temperatures not near the critical it is in fact constant. This work was continued with CO_2—Measurements on capillary ascension of liquefied carbonic acid near the critical temperature, *V.* **1896-97**, 94; *C. 28*, 1,—with which the density differences for the liquid and vapor were shown to be

$$\rho_l - \rho_v = A(1 - m)^{0.367}.$$

The derivative, of the logarithm, with respect to $\log(1 - m)$ rises o nearly the theoretical value for the critical point, and the corresponding derivative of the surface energy rises, after passing a minimum, to nearly its theoretical value there. In connection with all this compare the work of Ramsay and Shields. Verschaffelt's latest paper—On capillary ascension between two concentric cylindrical tubes, *V.* **1896-97**, 175; *C. 32*, 1—recalls that in his measurements with CO_2, which were made in a capillary tube within a wide enclosing tube, he had assumed the meridian section of the ring-shaped surface to be nearly an ellipse. The sufficiency of this assumption was then tested by finding the corresponding correction for outer tubes of various diameters, which, using CH_3Cl, gave very satisfactory results. The latest publications of these series are by A. van Eldik—Measurements of the capillary ascension of the liquid phase of a mixture of two substances in equilibrium with the vapor phase, *V.* **1897-98**, 18 and 74—whose work is related to Kuenen's studies on the dependence of the Waalsian constants upon the composition, as well as to Verschaffelt's measurements of capillarity. The variation of the capillary rise with changing pressure at constant temperature, for mixtures of methyl chlorid with ethylene, was determined at 10° and again at 23°, the pressures ranging from about 4 atm to the plaitpoint pressure in each case—nearly sixty atmospheres. Two curves show the change of height with pressure in each case, they intersect at 42.5 atm; the curve for methyl chlorid itself is also given. The behavior of such binary systems is supposed to resemble that of the non-normal substances under the van der Waals theory, which are supposed to be mixtures of simple and multiple molecules.

J. E. T.

Papers, from the University Laboratory of Physics at Leiden, on the Applications of Lorentz's Electromagnetic Theory of Light.

1. *Magnetic Rotation.* In his elctromagnetic optical theory H. A. Lorentz supposes light to proceed from the electrical vibration of light-ions. He supposes every light vibration to be composed of a right and a left circularly polarized ion vibration, different in phase and in amplitude, and that the ions are held in equilibrium by centripetal forces whose amount determines the velocity of the circular vibration. In a magnetic field the ions are then acted upon by an electrodynamic force, perpendicular to the magnetic force and to the momentary ion-velocity, so that, depending upon the direction of the circular motion, the centripetal force is either helped or hindered and the velocities of the two circularly polarized rays are made different,—*i. e.* a ray parallel to the magnetic force would get a rotation of its plane of polarization. L. H. Siertsema—*V.* **1893-94**, 31 ; *C. 7*, 9. *V.* **1894-95**, 230 ; *C. 15*, 14. *V.* **1895-96**, 294 and 317 ; *C. 24*, 1 and 12. *V.* **1896-97**, 131 and 132 ; *C. 31*, 1 and 5. *V.* **1896-97**, 305 ; *C. 35*, 1. *V.* **1897-98**, 24 ; *C. 38*, 1—has long worked upon the experimental confirmation of this theory, using chiefly oxygen under about 100 atm pressure. Other gases were examined also, and much time was required for questions of dispersion, *etc.* For low concentrations, only, the natural rotation of solutions of cane sugar was found to change in proportion to the pressures, and the conclusion was reached that the variation of specific rotation, through change of pressure or of concentration or through addition of a salt, is more complicated than is assumed in the hypothesis of Tammann. In 1896 Onnes—*V.* **1895-96**, 311 ; *C. 25*, 1—described an ingenious device for reading illuminated scales, which has been employed in the above and in many other important researches.

2. *Kerr Effect.* In order to get a measurable magnetic rotation in gases the length of tube must be considerable. In magnetic metals, indeed, the rotation is great, but the transparency is slight. To avoid these difficulties R. Sissingh undertook a study of the related Kerr's phenomenon, *i. e.* rotation upon reflection from a magnetic surface. The theoretical relation between the two, as outlined by Lorentz and elaborated by van Loghem (1883), is as follows : The motion of the ions in the reflecting surface must be made up of mo-

tions which correspond to those in the incident and reflected rays and to those in the refracted ray ; the peculiarities of the transmitted light must therefore appear also in that which is reflected. But, the velocities and absorptions of the right and of the left vibrations being changed differently by the electromagnetic force, it follows that with parallel, linear polarized light, the reflected ray has one component polarized like the incident ray, and another—the magneto-optic component—polarized perpendicularly thereto. This component must have a definite small amplitude and a definite phase different from that of ordinary reflected light, and it causes on the whole a rotation of the reflected light—the Kerr effect. Sissingh—Dissertation, Leiden, 1885 ; *C. 1*, 1 ; *Arch. néerl.* **20**, 171. *Verh. Akad. Amst.* 1890 ; *C. 3*, 1 ; *Wied. Ann.* **42**, 115 (1891) ; *Phil. Mag.* 5, **31**, 293 (1891)—measured this phenomenon accurately, finding for iron a phase difference varying from the theoretical, the variation being independent of the angle of incidence. P. Zeeman—*V.* **1892-93**, 19 and 58 ; *C. 5*, 1 and 7 ; *Arch. néerl.* **27**, 252, (1893). *V.* **1893-94**, 82 ; *C. 8*, 1. *V.* **1893-94**, 174 ; *C. 10*, 1. *V.* **1894-95**, 221 and 230 ; *C. 15*, 1 and 13—and C. H. Wind—*V.* **1893-94**, 116 ; *C. 9*, 1—thereafter found the same thing for Ni and Co as well as for Fe, Zeeman incidentally showing—*V.* **1895-96**, 116 ; *C.* 20, 1—that the refractive index of Pt does not change with the temperature. Wind then brought the theory into harmony with the observations, by supposing that the electrodynamic force is not the same for the ions whose motion effects electrical conductivity, as for those whose motion gives Maxwell's displacement currents. He concluded further that magnetization perpendicular to the surface of incidence, as well as magnetization parallel thereto, should give a magneto-optic effect, and he assigned the sign and amount of the new effect. This forecast was thereupon confirmed by Zeeman—*V.* **1896-97**, 103 ; *C. 29*, 1. There remain two papers by Wind—*V.* **1897-98**, 92—and by Lorentz—*V.* **1897-98**, 94—giving theoretical deductions of formulas for the dispersion of magnetic rotation in dielectrics.

3. *Damping of Waves.* Cohn and Zeeman.—*V.* **1895-96**, 108 ; *C. 21*, 1 ; *Wied. Ann.* **57**, 15 (1896)—proved that electrical waves, of frequency from 27 to 97 millions, show no dispersion in water, and that their refractive index is the square root of the dielectric constant. Zeeman then—*V.* **1895-96**, 148 and 188 ; *C. 22*, 1 and 10. *V.*

1896-97, 133 ; *C. 30*, 1—showed that electrical waves are damped in aqueous electrolytes, that solutions of equal conductivity absorb alike vibrations of the same period, that with given wave length the coefficient of absorption is approximately proportional to the square root of the conductivity, and that increasing both wave length and conductivity in the same ratio leaves the absorption unaltered.

4. *Magnetization and Emission.* Zeeman's studies on the Kerr effect led him to try the effect of strong magnetic fields upon the emission of light ; he found such fields to broaden the spectrum lines of incandescent sodium vapor, and he saw in this an effect of the electrodynamic force in changing the periods of the right and the left ions. Lorentz, in this manner, predicted that the edges of the broadened line must be polarized in a definite way, which Zeeman confirmed—*V.* **1896-97**, 181 and 242 ; *C. 33*, 1 and 9 ; *Arch néerl.* (2) **1**, 44 (1897) ; *Phil. Mag.* (5) **43**, 226 (1897) ; *Astrophys. Jour.* **5**, 332 (1897). E. van Aubel then stated—*V.* **1896-97**, 356—that C. Fievez had earlier found emission spectra to be modified by magnetism, and had thought reversals were produced ; he observed no modification of absorption spectra. Hereupon A. A. Michelson—*Astrophys. Jour.* **6**, 48 (1897)—using his interferometer, found the magnetization to separate the Na, the red and the green Cd and the green Hg lines each into two components of equal intensity, and with almost no broadening in the first two cases. With the double lines of H, Li and Tl he found further separation, with slight broadening. With Na the broadening disappeared when the light was parallel with the magnetic field. Fievez's reversals apparently do not occur.

5. *Hall Effect.* When the electrical conductivity of a metal is ascribed to the transfer of charges by moving ions, it is seen that in a magnetic field the electrodynamic force will displace each ion and thus rotate the potential surfaces. This effect is measured by the Hall coefficient. Measurements of the effect with Bi and Sb, including observation of a temperature coefficient, of a dissymmetry—the effect having different strengths for opposite directions of magnetizing—and of its variation with resistance and crytalline state, and the proof that the resistance of Bi in a magnetic field does vary in different directions, have been made by A. Lebret—*V.* **1894-95**, 238 ; *C.*

15, 28. *V.* **1894-95**, 284 and 292; *C. 19*, 1 and 17. Dissertation, Leiden, 1895; *V.* **1895-96**, 103; *C. 19*, 25—and by E. van Everdingen Jr.—*V.* **1896-97**, 47 and 51; C. *26*, 1 and 10. *V.* **1896-97**, 492 and 494. *V.* **1897-98**, 68. *J. E. T.*

On the Dielectric Constant of Ice and Alcohol at very Low Temperatures. *J. Dewar and J. A. Fleming. Proc. Roy. Soc.* **61**, *2* (*1897*). For water at about zero, the dielectric constant seems to have a value of 80, which is independent of the frequency of discharge. This is not the case with ice, the value just below zero being about 78 when using very slow oscillations and about 2.0 when using oscillations having a frequency of some millions per second. The authors have determined the dielectric constant for ice at low temperatures with 124 oscillations per second. At — 130.7° they find 11.6 and at — 198.0 only 2.83. From the curve it would appear that at the absolute zero the value would be 2.0. Alcohol at — 185° gives 3.12. The condenser consisted of three concentric brass tubes and a galvanometer was used to measure its capacity. Measurements are also given for the variations of the resistance of an ice or alcohol condenser at low temperatures. *W. D. B.*

On a Method of Determining the Dielectric Constants of Solids. *H. Starke. Verh. phys. Ges. Berlin*, **15**, *69*; *Wied. Ann.* **60**, *629* (*1897*). The method consists in mixing two liquids in such proportions that the mixture has the same dielectric constant as the solid under investigation. The dielectric constant of the solution can then be determined in the ordinary way. Data are given for glasses, woods and some miscellaneous solids. *W. D. B.*

Conductivity of Carbon for Heat and Electricity. *L. Cellier. Wied. Ann.* **61**, *511* (*1897*). It was shown by H. F. Weber in 1880 that, for any metal, the ratio of the coefficient of conductivity for heat to the electrical conductivity is a linear function

$$K_w/K_e = a + bc_1,$$

with constant coefficients, of the heat capacity of the unit volume. In the present paper this ratio is determined experimentally for rods and prisms of graphite, of arc carbon and of gas-retort carbon; it was found to vary from 1.8×10^6 to 53.7×10^6, from which was concluded that Weber's relation holds only for metals. *J. E. T.*

THE ELECTROLYSIS AND ELECTROLYTIC CONDUCTIVITY OF CERTAIN SUBSTANCES DISSOLVED IN LIQUID AMMONIA

BY HAMILTON P. CADY

The remarkable similarity existing between certain crystalline salts containing water of crystallization and similar salts containing ammonia, has suggested the idea that perhaps water and ammonia might be analogous in some of their other properties. Acting on this suggestion it was thought best to test the dissociative power of liquid ammonia, on dissolved substances.

The only record that could be found of any work bearing directly on this subject, was a statement by Dr. L. Bleekrode,[1] that liquid ammonia was a good conductor of electricity, and that while the current was passing the liquid turned blue, and became colorless again when the current ceased, Weyl,[2] and G. Gore,[3] investigated the action of various substances, dissolved in liquid ammonia, upon each other, but they seem not to have tried the conductivity of such solutions.

The liquid anhydrous ammonia used in the following experiments, was the ordinary commercial ammonia used in the manufacture of ice, and proved to be of sufficient purity for the purpose. The experiments were made in vacuum-jacketed test tubes, which were made in our laboratory by Prof. E. C. Franklin, and answered admirably for the purpose. This may be illustrated by the fact that 15 cc. would not all evaporate inside of three hours, at the ordinary temperature. The test tubes were fitted with a doubly-bored cork stopper, through one of the holes of which the ammonia was led in,

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[1] Phil. Mag. [5] **5**, 384 (1878).

[2] Pogg. Ann. **121**, 601 ; **123**, 350 (1864).

[3] Proc. Roy. Soc. **20**, 441 (1872).

while the uncondensed gas was allowed to escape through a long glass tube, inserted into the other opening and bent at right angles. This arrangement protected the ammonia from moisture while it was being drawn from the cylinder. During the experiment the ammonia was protected by a calcium chloride tube, filled with soda lime.

The electrodes used in the experiments on electrolysis, were simply platinum plates held in position by glass rods, fused to the leading-in wires. When pure ammonia was submitted to the action of a battery of six storage cells having a potential of 12 Volts, no signs of a current could be detected. Even with a potential of 110 Volts and electrodes 1 cm. apart, and having an area of 25 square cm., only a few hundredths of an ampere passed through. The liquid did not turn blue, but simply boiled vigorously. If however a small quantity of a soluble salt be added to the ammonia the solution becomes an excellent conductor, and in the case of the sodium or potassium salts, the solution turns blue, if the 110 volt current be used, but it becomes colorless again when the current is shut off.

This furnishes an explanation for the difference between these results and those obtained by Dr. Bleekrode, l. c. His ammonia was prepared as follows: «The chlorides of silver and calcium were saturated with the gas; and with them quicklime and sodium were enclosed in the condensation tube, in order, on expelling the gas by heating, to remove the last traces of water. The separated liquid ammonia was several times poured back over the sodium, by inverting the tube, and redistilled». Evidently the ammonia had become contaminated with some of the sodium hydroxide, formed by the action of water on sodium. This makes a solution that conducts readily and the sodium set free at the cathode dissolves, forming a bright blue solution, the color disappearing when the current is shut off. Dr. Bleekrode ascribed the blue coloration to the formation of free ammonium, NH_4, according to the reaction $2NH_3 = NH_4 + NH_2$.

Weyl l. c. describes the formation of ammonium by the action of a solution of sodium upon ammonium chloride or sulphate. He obtained a bright blue liquid that rapidly decomposed into ammonia and hydrogen. Since the solution of sodium in ammonia is also bright blue, it would appear to be difficult to say just when the color was due to sodium and when it was caused by free ammonium. If an excess of ammonium bromide or iodide, both of which are very soluble in ammonia, be added to a solution of sodium in that menstrum, the blue color is instantly destroyed, and at the same time hydrogen is evolved. With ammonium chloride or sulphate the action is the same only slower, as these salts are not very soluble in ammonia.

If an electric current of 110 volts be passed through a solution of an ammonium salt in ammonia, there is a violent evolution of gas, but no signs of a blue coloration. In neither of these experiments could any evidence of a blue coloration that might be ascribed to the presence of free ammonium, be detected.

If a current of varying strength, up to 110 volts be passed through solutions of salts of silver, copper, or barium, the metals are deposited upon the cathode, but there is no sign of a blue color. If sodium be added to a solution of one of these salts the metal is precipitated but no blue color appears until an excess of sodium is present. Weyl, thought that he had obtained a blue solution of ammonium compounds of these metals by the action of sodium solution on their chlorides according to the reaction—

$$N_2H_6Na_2 + 2NH_3 + BaAl_2 = N_2H_6Ba + 2NH_3NaCl.$$

According to Weyl these ammonium compounds easily decompose into ammonia and the metal. Their existence is not confirmed however by the above experiments. The blue color observed by Weyl was due perhaps to the presence of free sodium. In every case he used chlorides of the metals, and these being only slightly soluble the action of the sodium would be relatively slow.

If potassium iodide be dissolved in ammonia and a current of from six to twelve volts be passed through the solution, electrolysis takes place, hydrogen is evolved and a deposit collects on each electrode. On the cathode the deposit is dark gray and reacts violently with water, giving a hissing sound and ammonia and potassium hydroxide are formed. The deposit probably consisted of potassium amide KNH_2, but a sufficient quantity for analysis could not be obtained. If the current be passed in series through the potassium iodide solution and through an apparatus for the generation of electrolytic gas, the ratio of the hydrogen from potassium iodide solution, to the mixed electrolytic gas was not that required by theory, but the volume of hydrogen was always too small. That the gas was hydrogen was proven by exploding it with oxygen.

The deposit on the anode varied from bluish black to olive green. It was insoluble in water but soluble in ether, alcohol and chloroform, and in potassium iodide solution, in each case with the evolution of gas. It explodes violently on heating, by friction and on contact with acids. The same substance was formed in the electrolysis of several other iodides. It was impossible to obtain enough of this compound to use for analysis, but it agrees closely in physical and chemical properties with the compound formed by the action of iodine on liquid ammonia, and which has the composition HN_3I, as noted in a previous article.[1]

Mercuric iodide dissolves easily in ammonia. The solution conducts readily, and the products of electrolysis are mercury and the explosive compound of iodine noted above.

Silver nitrate is also readily soluble and the solution is a good conductor. Metallic silver is deposited on the cathode.

Lead nitrate is easily soluble and the solution is a moderately good conductor, while metallic lead is deposited.

The behavior of a solution of sodium in ammonia is quite remarkable; the solution is an excellent conductor. There is no deposit on the electrodes; no gas is evolved, and the blue color of the sodium is not altered by the passage of an enormous quantity of electricity. If only a little sodium is present the color becomes more intense around the cathode. There is no polarization current.

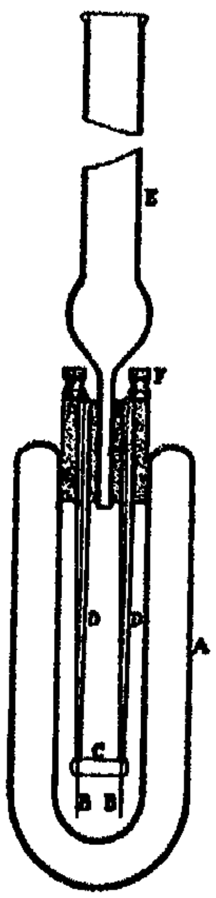

FIG. 1

FIG. 2

In the experiments on conductivity the following apparatus was used :—

«A» is a vacuum jacketed test-tube. It is graduated so that

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[1] Kan. Univ. Quar. Vol. VI, No. 2, p. 71 (1897).

the volume of the ammonia can be read directly. B B are the electrodes, consisting of a stout platinum foil welded to strong platinum wires and held in position by the glass rod C which is fused on to the wires. The wires that conduct the current are insulated by the slender glass tubes D D, the lower ends of which are fused on to the wires, and the latter are connected with the binding posts F F. E is a calcium chloride tube filled with soda lime. Fig. 2 is a side view of the electrodes and connections.

The results given below are preliminary and are not regarded as possessing any very great accuracy; they are however close enough to settle the question as to whether or not ammonia possesses the power of dissociating dissolved substances to a degree comparable with water. The chief sources of error that have not been fully overcome, are the impossibility of preventing boiling at the electrodes which increases the apparent resistance and consequently lowers the molecular conductivity; the difficulty of accurately controlling the dilution on account of the evaporation of the ammonia; and finally the slight impurity of the ammonia. This latter of course increases the error in the determination of substances that are only slightly dissociated.

The presence of a small amount of water does not seem to have a measurable effect on either the conductivity of ammonia alone or of solutions of substances dissolved therein. The ammonia used had a conductivity of 71×10^{-7}.

Mercuric nitrate is not completely soluble, as a yellow compound resembling basic nitrate separates out, so no determination could be made.

In the case of the sodium solution, no signs of a polarization current could be detected with a sensitive galvanometer, and it will be noticed that the molecular conductivity rises with the concentration, contrary to that of electrolytes. As has been mentioned above no gas is given off when the solution is submitted to electrolysis. The sodium is not affected by the current, nor is there any deposit on the electrodes. In spite of the fact that the sodium is in solution, the solution seems to conduct like a metal and not like an electrolyte.

In this connection it is interesting to note that J. J. Thomson has shown that the vapor of sodium is a conductor, a result that we had also obtained before learning of his researches.

Salt used	Dissolved in ammonia at −34°		Dissolved in water		
	V	μ	V	μ	
Potassium chloride	Not sufficiently soluble				
Potassium iodide,	80.	169.	100.	116.	at 18°
	100.	178.			
	110.	179.			
Potassium bromide,	100.	169.	128.	117.	at 18°
	120.	179.			
	135.	181.			
Potassium nitrate,	80.	123.	100.	114.	at 18°
	100.	124.			
	120.	131.			
Ammonium chloride,	40.	96.5	55.7	105.	at 18°
	50.	98.5			
	55.	99.			
	61.5	103.			
Ammonium bromide,	40.	124.			
	50.	132.			
	57.5	143.			
	67.5	144.			
Ammonium iodide,	40.	146.			
	50.	155.			
	60.	173.			
Sodium bromide,	140.	154.	128.	115.8	at 25°
	150.	158.			
Sodium iodide,	150.	166.	128.	112.3	at 25°
Silver nitrate,	140.	147.	166.	103.3	at 18°
Mercuric iodide,	150.	102.			
Mercuric cyanide,	130.	39.			
Lead nitrate,	105.	77.			
	130.	88.			
Metallic sodium,[1] 23 being taken as the molecular weight,	4.28	393.			
	3.97	413.			
	3.8	448.			

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[1] These results are somewhat low, because the ammonia contained some water. This of course would react with the sodium and form sodium hydroxide, which has a much lower conductivity than sodium.

In conclusion it may be said that ammonia seems to possess the power of dissociation of dissolved substances to as great an extent as water, and in most cases the ions seem to travel even faster in it than in water. It would seem, furthermore, that water and ammonia do resemble each other in their power to dissociate dissolved substances, as well as in their ability to unite directly with certain metallic salts.

It is proposed to continue this work with improved apparatus, and it is hoped that greater accuracy may be attained.

ON A NEW FORM OF CONSTANT VOLUME AIR THERMOMETER, WHICH SHOWS THE TOTAL PRESSURE DIRECTLY, AND MAY BE GRADUATED IN DEGREES BY TEMPERATURE[1]

BY J. R. ERSKINE MURRAY

§ 1. The thermometer described in the present communication is a constant volume one. Its advantages proceed mainly from a simple arrangement whereby the total pressure of the enclosed air, and hence its temperature, since these are proportional, is measured directly by the height of one column of mercury. The external atmospheric pressure is eliminated by the adjustment of an auxiliary reservoir of mercury.

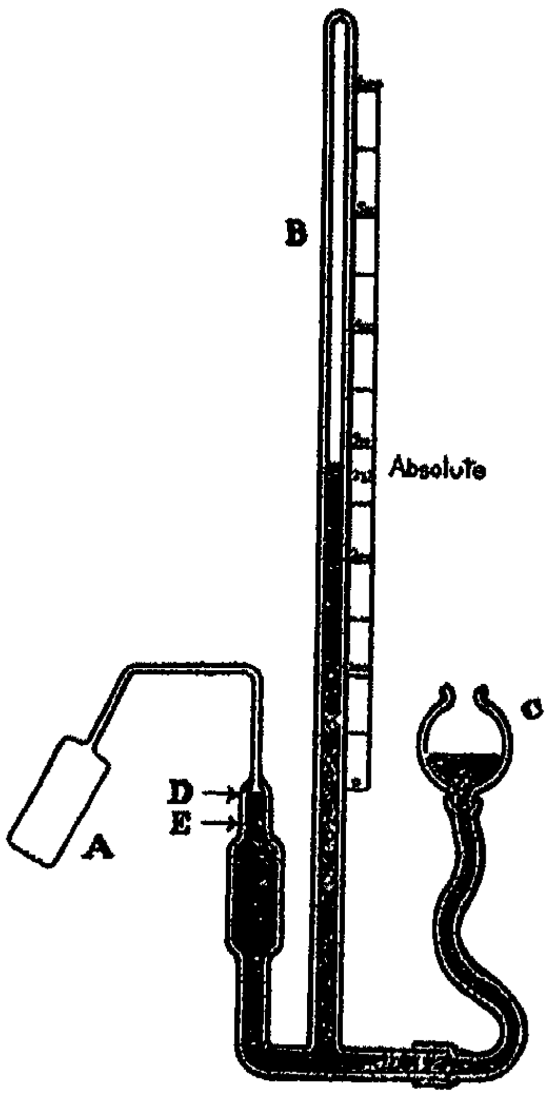

FIG. 1

§ 2. In Fig. 1, A is the air-bulb, B is the pressure-gauge, which is an ordinary barometer tube with a vacuum above the mercury connected at its lower end to the bent stem of the air-bulb and also by a flexible tube to the reservoir C. D is the constant volume mark on the stem of the air-bulb. The part of the instrument which is filled with mercury when the air is at 0° C is shaded in the diagram.

§ 3. To make an observation of temperature the mercury is adjusted to the mark D by raising or lowering the reservoir. The

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[1] From the Proc. Roy. Soc. Edinb. **21**, 299 (1897).

height of the column in B above the level of the mark D now gives the total pressure of the enclosed air. The air-bulb and pressure gauge may be cut off entirely from external pressure by closing the stop-cock between the pressure-gauge and the reservoir. If the absolute temperature corresponding to any given value of the pressure be known, we can calculate that corresponding to any other pressure by simple proportion.

Thus, in order to graduate the thermometer in degrees of temperature, it is only necessary to find the total pressure for any one temperature; that of melting ice, which we may take as 273° on the absolute scale of temperature, is the most convenient. To fix this point on the scale, the bulb is immersed in melting ice and the mercury adjusted to the volume mark by raising or lowering the reservoir. The height, h, of the mercury column in B above the level of the mark now corresponds to 273° absolute. But, since pressure and temperature are in simple proportion, the degrees at all parts of the scale are of equal length; thus $h/273$ is the length of one degree.

§ 4. It will be seen that the reservoir is merely a device for supplying mercury at the proper pressure to fill up the gauge-tube, and that it may be replaced by any suitable mechanical device, such as a cylinder full of mercury in which a piston is forced down by a screw. It is obvious that the height of the mercury in B above its level in the open reservoir C always corresponds to the atmospheric pressure at the moment. This portion of the apparatus is in fact a barometer if the reservoir C be open, but it is not in the least essential that it should be so.

§ 5. The atmospheric pressure is, after all, merely an *accident;* and its constant recurrence in all calculations on the pressure of gases is very misleading to the student, who is apt to look upon it as a factor of a different nature to the observed pressure in the ordinary air thermometer, and hinders his realization of the fact of the simple proportionality of temperature and pressure or volume.

§ 6. The length of a degree on this thermometer depends only on the total pressure at some given temperature; hence it is clear that the sensibility of the thermometer may be altered to suit any purpose by choosing a proper pressure at which to fill the bulb with air at the standard temperature. Thus, if great sensibility be required, the air when immersed in melting ice should be under great pressure, making the height *h*, which is equivalent to 273°, large; while, if a great range of temperature be required without great sensibility, it is only necessary to partially exhaust the bulb, at the same time placing the reservoir *below* the volume mark, so that the atmospheric pressure may be partially counterbalanced.

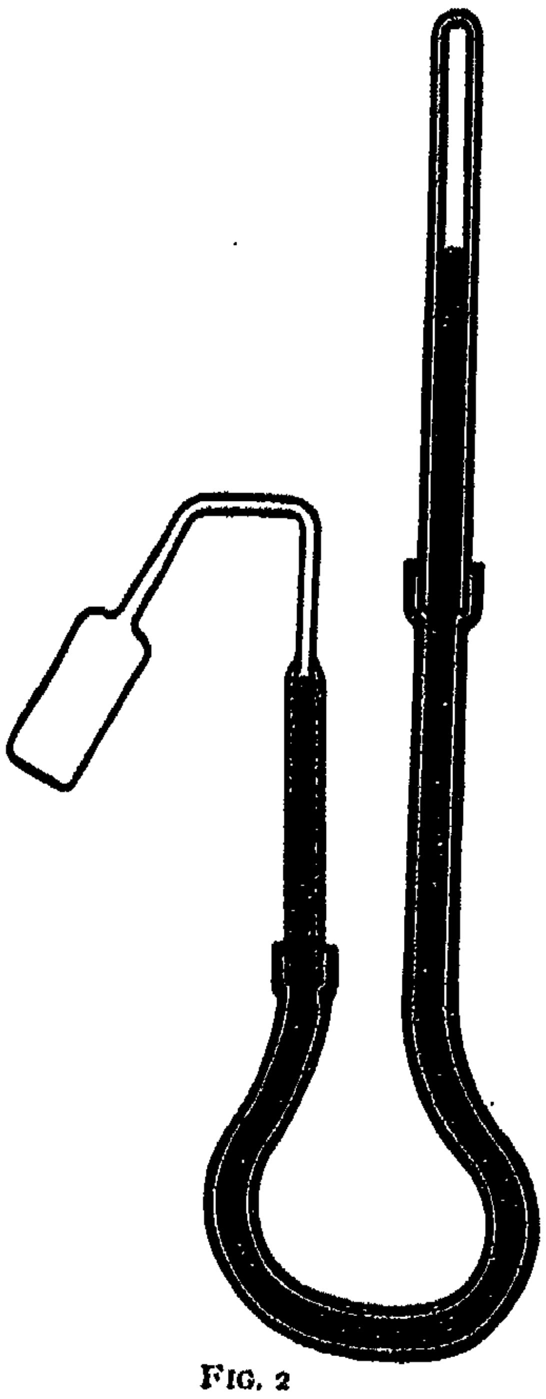
FIG. 2

The length of the pressure-gauge tube of the thermometer may thus be indefinitely reduced, though of course at low pressures the open reservoir would require to be placed at nearly the barometric height below the volume mark.

The easiest way to obtain at 0°C. at a pressure somewhat below that of the atmosphere is to fill the bulb with air at a high temperature, balancing the reduction of pressure and maintaining the volume constant as it cools by lowering the reservoir. When at 0°C the air will now have a pressure below that of the atmosphere.

§ 7. In order to facilitate the correction for capillarity, on account of difference in the diameters of the pressure-gauge tube and the volume-gauge, the constant volume mark may be put in at the end of the fine tube at the stem, just where it joins the wider tube which forms its downward continuation. At this point the tube is conical, and its walls make an angle of about 45 degrees with the horizontal. Hence the mercury surface when at this point will be a plane, and its surface tension will act entirely in a horizontal direction.

§ 8. In order to be able to adjust the quantity of air in the bulb while filling it, a small capillary, E, is drawn out from the side of the stem at a point near the volume mark. This allows the air to escape as the mercury is introduced. The capillary is sealed before the reading of the pressure at 0°C is taken.

§ 9. It would be possible to give the thermometer a greater apparent simplicity by omitting the auxiliary reservoir and making the pressure-tube movable, as in Joly's thermometer. The simplification is more apparent than real, however, and introduces several disadvantages. It would be impossible to graduate the pressure-tube itself, and hence some other arrangement would have to be used. The clamp which supported the main tube would also have to be in a more inconvenient position than that for the reservoir in the form in which I have described (see fig. 2).

PRECIPITATION OF SALTS

BY A. ERNEST TAYLOR

At the suggestion of Prof. Bancroft I have undertaken a few experiments on the precipitation of salts from aqueous solutions by alcohol or acetone. Work exactly similar to this has recently been done by Bathrick.[1] He found that his results could be expressed by an equation of the general form $(x+A)y^n = C$, where x and y represent respectively the weight of alcohol and of salt in a fixed weight of water. Bancroft[2] had previously used this equation to describe the solubility of various salts in alcohol containing varying percentages of water, as taken from the data given by Gérardin[3] and Bodländer.[4]

The method of experimentation which I employed was very much the same as that used by Bathrick. The alcohol, which at first contained but a trace of water, was distilled from lime; then after standing over dehydrated copper sulphate for a day or two was again distilled. This last operation was usually repeated. Copper sulphate was added as long as any blue color was perceptible. This alcohol, as soon as distilled, was immediately made up gravimetrically into solutions containing from ten to ninety-five percent of water, care being taken that the solutions be accurate within a few hundredths of a percent. These solutions were then preserved in carefully stoppered bottles, which had been thoroughly cleaned and boiled out with steam. Small bottles, similarly cleaned, were used for the solubility determinations. At first glass stoppers were tried, but rubber stoppers seemed to prevent more effectually any error

[1] Journ. Phys. Chem. **1**, 156 (1896).
[2] Ibid. **1**, 33 (1896).
[3] Ann. Chim. Phys. (4) **5**, 129 (1865).
[4] Zeit. phys. Chem. **7**, 308 (1891).

from evaporation. When solutions of acetone were used, cork stoppers were substituted. These small bottles, containing the aqueous alcohol and a large excess of very finely powdered salt, were placed in an Ostwald thermostat for about half a day at a temperature some ten degrees higher than that at which the solubility was to be determined. During this time the bottles were shaken frequently and thoroughly. The temperature was then lowered and carefully maintained at the desired point for about a day, at the end of which time a measurement was made, and repeated two or three times at intervals a day apart. In no case did I observe any trace of supersaturation. At first I made up my solutions at the desired temperature, making a measurement at the end of a day, as described by Bathrick. This did not give me accurate results, for on repeating the measurements I found the solubility to increase. In some cases it approached very nearly a constant at the end of three days; but, at least six days were required for many measurements. I determined the solubility of sodium chloride at 40° by both methods, and found the results to agree well. The last method, however, admits of much more possibility of error from evaporation and other causes, by reason of the greater length of time required. With potassium bromide I found it almost impossible to determine the saturation point by this method.

The salts used were all from Bender and Hobein, and of the purest quality marked Ph. III, with the exception of the potassium chlorate. The sodium chloride and potassium bromide were simply fused after being tested for impurities. The sodium nitrate and potassium chlorate were recrystallized two or three times and dried in an air bath. I could detect no trace of nitrite in the sodium nitrate after drying, nor in the solutions after the solubility had been determined. The aqueous solutions of acetone were made up by Mr. Snell, the acetone used having been prepared with great care so that it distilled within a fraction of a degree.

The solubilities were determined by taking out about 5 cc of the saturated solution, weighing it and then determining the amount of salt left on evaporation according to the method described by Trevor.[1]

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[1] Zeit. phys. Chem. 7, 468 (1891).

The pipette used for taking out the solutions was usually warmed to prevent any precipitation of salt in it. The weighings were made accurate to a milligram. The values determined for the amount of salt in one gram of solution seldom varied more than a milligram, and in case the solubility was not too great the values obtained were somewhat more accurate than that. The values for the amount of salt in one gram of water, of course, had a somewhat greater error, increasing with the concentration of the alcohol. Measurements were made at 30° and at 40° with aqueous solutions of alcohol and acetone. The results are given in Tables I–X. In the first column are given the percentages by weight of alcohol or acetone in the aqueous solutions; in the second and third the weight of salt contained in one gram of saturated solution, as calculated and as observed respectively; in the third and fourth, the amount of salt contained in one gram of water, as calculated and as observed. The amount of alcohol in one gram of water is represented by x, the amount of salt in one gram of water by y and in one gram of saturated solution by y^1. When two formulae are used to represent the results given in any one table, the second formula always refers to the results which come below the dotted line.

TABLE I

Alcohol: $KClO_3$ at 30°

$$(x + 0.20)\, y^{1.57} = C_1 \quad \log C_1 = 7.740-10$$
$$(x + 0.20)\, y^{1.3} = C_2 \quad \log C_2 = 8.310-10$$

% Alc.	y¹ calc.	y¹ obs.	y calc.	y obs.	log C.
0	0.0920	0.0923	0 1013	0.1017	7.741–10
5	0.0767	0.0772	0.0874	0.0880	7.746–10
10	0 0644	0.0644	0.0765	0.0765	7.741–10
20	0.0460	0.0451	0.0604	0.0590	7.723–10
30	0.0331	0.0321	0.0489	0.0474	7.719–10
40	0.0234	0.0235	0.0398	0.0400	7.743–10
50	0.0165	0.0164	0.0335	0.0333	8.306–10
60	0.0101	0.0101	0.0251	0.0253	8.314–10
70	0.0054	0.0054	0.0180	0.0182	8.316–10
80	0.0024	0.0024	0.0118	0.0122	8.327–10
90	0.0006	0.0006	0.0061	0.0062	8.315–10

TABLE II

Alcohol : $KClO_3$ at 40°

$(x + 0.22)y^{1.57} = C_1$ $\log C_1 = 8.000-10$
$(x + 0.22)y^{1.2} = C_2$ $\log C_2 = 8.518-10$

% Alc.	y^1 calc.	y^1 obs.	y calc.	y obs.	log C.
0	0.1227	0.1223	0.1397	0.1393	7.999-10
5	0.1039	0.1048	0.1219	0.1233	8.008-10
10	0.0884	0.0884	0.1076	0.1077	8.001-10
20	0.0643	0.0640	0.0861	0 0856	7.996-10
30	0.0463	0.0467	0.0693	0.0700	8.007-10
40	0.0333	0.0341	0.0574	0.0588	8.016-10
50	0.0241	0.0241	0.0494	0.0494	8.519-10
60	0.0146	0.0146	0.0371	0.0369	8.516-10
70	0.0079	0.0078	0.0266	0.0263	8.511-10
80	0.0034	0.0034	0.0175	0.0173	8.511-10
90	0.0009	0.0012	0.0091	0.0117	8.647-10

TABLE III

Acetone : $KClO_3$ at 30°

$(x + 0.20)y^{3.6} = C_1$ $\log C_1 = 5.727-10$
$(x + 0.20)y^{1.55} = C_2$ $\log C_2 = 8.240-10$

% Acet.	y^1 calc.	y^1 obs.	y calc.	y obs.	log C.
0	0.0923	0.0923	0.1017	0.1017	5.727-10
5	0.0830	0.0832	0.0953	0.0956	5.732-10
9.09	0.0763	0.0763	0.0909	0.0909	5.728-10
20	0.0611	0.0609	0.0812	0.0810	5.724-10
30	0.0493	0.0493	0.0740	0.0740	5.727-10
40	0.0390	0.0390	0.0676	0.0676	5.726-10
50	0 0300	0.0290	0.0618	0.0598	5.675-10
60	0.0205	0.0203	0.0520	0.0517	8.236-10
70	0.0119	0.0124	0.0402	0.0418	8.267-10
80	0.0057	0.0057	0.0290	0.0288	8.235-10
90	0.0018	0.0018	0.0175	0.0182	8.267-10

TABLE IV

Acetone: $KClO_3$ at 40°

$(x + 0.22)\,y^{3.6} = C_1 \quad \log C_1 = 6.260-10$
$(x + 0.22)\,y^{1.55} = C_2 \quad \log C_2 = 8.475-10$

% Acet.	y' calc.	y' obs.	y calc.	y obs.	log C.
0	0.1223	0.1223	0.1393	0.1393	6.260–10
5	0.1111	0.1110	0.1312	0.1311	6.259–10
9.09	0.1025	0.1028	0.1255	0.1260	6.266–10
20	0.0828	0.0827	0.1128	0.1126	6.258–10
30	0.0670	0.0669	0.1026	0.1024	6.258–10
40	0.0536	0.0536	0.0945	0.0945	6.259–10
50	0.0415	0.0403	0.0865	0.0840	6.214–10
60	0.0285	0.0286	0.0732	0.0735	8.478–10
70	0.0168	0.0168	0.0567	0.0568	8.476–10
80	0.0080	0.0079	0.0410	0.0397	8.453–10
90	0.0024	0.0024	0.0247	0.0245	8.465–10

TABLE V

Alcohol: $NaNO_3$ at 30°

$(x + 0.70)\,y^{1.2} = C \quad \log C = 9.827-10$

% Alc.	y' calc.	y' obs.	y calc.	y obs.	log C.
0	0.4913	0.4910	0.9660	0.9645	9.826–10
5	0.4632	0.4641	0.9085	0.9115	9.828–10
10	0.4347	0 4350	0.8545	0.8555	9 828–10
20	0.3744	0 3742	0.7485	0.7475	9.826–10
30	0.3125	0.3131	0.6495	0.6510	9.829–10
40	0.2490	0.2514	0.5530	0.5595	9.833–10
50	0.1875	0.1894	0.4615	0.4675	9.834–10
60	0.1296	0.1297	0.3720	0.3725	9.828–10
70	0 0785	0.0781	0.2845	0 2825	9.823–10
90	0.0107	0.0121	0.1080	0.1225	9.883–10

TABLE VI

Acetone: $NaNO^3$ at 30°

$$(x + 0.70)\, y^{2.16} = C_1 \quad \log C_1 = 9.811-10$$
$$(x + 0.70)\, y^{1.57} = C_2 \quad \log C_2 = 0.016$$

% Acet.	y¹ calc.	y¹ obs.	y calc.	y obs.	log C.
0	0.4910	0.4910	0.9645	0.9645	9.811-10
5	0.4696	0.4696	0.9320	0.9320	9.811-10
9.09	0.4519	0.4511	0.9065	0.9040	9.809-10
20	0.4010	0.4010	0.8370	0.8370	9.811-10
30	0.3510	0.3508	0.7725	0.7720	9.810-10
40	0.2979	0.2980	0.7070	0.7075	9.811-10
50	0.2422	0.2434	0.6400	0.6440	9.817-10
60	0.1851	0.1855	0.5680	0.5695	9.814-10
70	0.1315	0.1315	0.5050	0.5050	0.016
80	0.0710	0.0710	0.3820	0.3820	9.016
90	0.0235	0.0198	0.2405	0.2020	9.896-10

TABLE VII

Alcohol: $NaCl$ at 30°

$$(x + 0.53)\, y^{1.9} = C_1 \quad \log C_1 = 8.882-10$$
$$(x + 0.53)\, y^{1.1} = C_2 \quad \log C_2 = 9.460-10$$

% Alc.	y¹ calc.	y¹ obs.	y calc.	y obs.	log C.
0	0.2650	0.2650	0.3605	0.3605	8.882-10
5	0.2459	0.2459	0.3429	0.3430	8.882-10
10	0.2267	0.2266	0.3260	0.3257	8.881-10
20	0.1905	0.1905	0.2940	0.2940	8.882-10
30	0.1560	0.1567	0.2637	0.2653	8.887-10
40	0.1234	0.1245	0.2347	0.2370	8.889-10
50	0.0934	0.0934	0.2061	0.2060	8.881-10
60	0.0636	0.0636	0.1698	0.1696	9.459-10
70	0.0360	0.0368	0.1241	0.1275	9.473-10
80	0.0160	0.0156	0.0818	0.0795	9.446-10
90	0.0042	0.0043	0.0416	0.0430	9.476-10

TABLE VIII

Alcohol: NaCl at 40°

$$(x + 0.58)\, y^{1.9} = C_1 \quad \log C_1 = 8.929{-}10$$
$$(x + 0.58)\, y^{1.1} = C_2 \quad \log C_2 = 9.494{-}10$$

% Alc.	y^1 calc.	y^1 obs.	y calc.	y obs.	log C.
0	0.2668	0.2668	0.3639	0.3638	8.929-10
5	0.2482	0.2479	0.3475	0.3469	8.928-10
10	0.2302	0.2290	0.3323	0.3300	8.925-10
20	0.1942	0.1946	0.3012	0.3020	8.931-10
30	0.1601	0.1602	0.2721	0.2725	8.930-10
40	0.1273	0.1275	0.2431	0.2437	8.931-10
50	0.0969	0.0967	0.2146	0.2142	8.927-10
60	0.0665	0.0665	0.1782	0.1783	9.494-10
70	0.0378	0.0387	0.1310	0.1343	9.505-10
80	0.0171	0.0169	0.0869	0.0862	9.490-10
90	0.0044	0.0050	0.0445	0.0510	9.560-10

TABLE IX

Alcohol: KBr at 30°

$$(x + 0.42)\, y^{2} = C_1 \quad \log C_1 = 9.329{-}10$$
$$(x + 0.42)\, y^{1.3} = C_2 \quad \log C_2 = 9.700{-}10$$

% Alc.	y^1 calc.	y^1 obs.	y calc.	y obs.	log C.
0	0.4162	0.4162	0.7130	0.7130	9.329-10
5	0.3897	0.3898	0.6720	0.6725	9.330-10
10	0.3633	0.3633	0.6340	0.6340	9.329-10
20	0.3109	0.3109	0.5640	0.5640	9.329-10
30	0.2598	0.2598	0.5015	0.5015	9.329-10
40	0.2100	0.2124	0.4430	0.4495	9.341-10
50	0.1625	0.1627	0.3880	0.3885	9.331-10
60	0.1153	0.1150	0.3260	0.3250	9.698-10
70	0.0677	0.0690	0.2420	0.2470	9.711-10
80	0.0316	0.0309	0.1630	0.1595	8.689-10
90	0.0086	0.0087	0.0868	0.0880	9.705-10

TABLE X

Alcohol: KBr at 40°

$$(x + 0.50)y^2 = C_1 \quad \log C_1 = 9.468-10$$
$$(x + 0.50)y^{1.2} = C_2 \quad \log C_2 = 9.790-10$$

% Alc.	y^1 calc.	y^1 obs.	y calc.	y obs.	log C
0	0.4340	0.4340	0.7665	0.7665	9.468–10
5	0.4093	0.4085	0.7295	0.7270	9.465–10
10	0.3843	0.3831	0.6935	0.6900	9.464–10
20	0.3336	0.3327	0.6260	0.6230	9.464–10
30	0.2825	0.2832	0.5625	0.5645	9.471–10
40	0.2315	0.2322	0.5020	0.5040	9.472–10
50	0.1812	0.1811	0.4425	0.4425	9.468–10
60	0.1305	0.1302	0.3750	0.3740	9.789–10
70	0.0777	0.0798	0.2810	0.2890	9.805–10
80	0.0367	0.0365	0.1905	0.1895	9.787–10
90	0.0101	0.0103	0.1025	0.1045	9.801–10

I repeated the work of Bathrick on the solubility of sodium chloride, but the values of *n* and of *A* do not agree with those obtained by him, nor do his values of *n* and *A* for sodium nitrate at 40° with acetone and with alcohol agree with mine determined at 30°. It is difficult to determine the value of *A* with certainty, for unless all the measurements made are accurate it is possible to vary *A* considerably and still have the formula hold almost equally well in each case.

The constant *A* was found to be independent of the precipitating agent for any given salt and to vary only with the temperature. The constant *n*, however, seemed to be independent of the temperature, but to vary with the precipitating agent. These observations simply confirm the conclusions of Bathrick.

It will be seen that, in every case but one, two equations are needed to express the solubility. Bancroft considers that this indicates a change from water as the solvent to alcohol or acetone as the solvent. In almost every case the break comes between fifty and sixty percent alcohol, in some cases between forty and fifty percent.

That is, when the aqueous alcohol contains less than fifty percent of alcohol, the water contained acts as the solvent; but when more alcohol is contained, then alcohol acts as the solvent. The values on the last curve are not as accurate as those on the first part, for the value y, the weight of salt in one gram of water, is not as accurately determined in solutions containing a large percentage of alcohol. The values of y^1, the amount of salt in one gram of saturated solution is determined directly, and a rather large error may be introduced when we change to y, as for instance in the ninety percent alcohol, when five grams of solution contain only about half a gram of water. Therefore, although y is used directly in the equation, we must compare the values of y^1, as determined by experiment and as calculated from the formula, if we would judge correctly of the accuracy with which the equation states the facts obtained by experiment.

Thus far we have been dealing with the equilibrium between three substances; a solid and a liquid which are non-miscible, and water which is consolute with the liquid, but only partially miscible with the solid. If for the liquid another solid with a limited solubility in water be substituted, a similar equation $(x + A)(y + B)^n = C$ may be used, having one more constant. The constants, A and B, however, are exactly the same as the constants A and A^1 obtained from solubilities of the first type. Using this general formula Bathrick tabulated the results of Nicol[1] on the solubility of mixtures of sodium and potassium chloride and of sodium chloride and nitrate. As I did not obtain the same values for A that he did in the equations representing the solubility of sodium chloride and sodium nitrate in aqueous alcohol, I have recalculated the work of Nicol and find that I obtain as good an agreement with the values given by experiment as is obtained by Bathrick, and in some cases a better one. These results are given in Tables XI–XIV. I used the constant 18 determined by Bathrick for potassium chloride.

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[1] Phil. Mag. [5] 31, 369 (1891).

TABLE XI

NaCl at 20°

x = g. $NaNO_3$ y = g. NaCl

$(x + 50)(y + 60)^{6.8} = C_1$

$\log C_1 = 15.175$

x	y calc.	y obs.
0.0	35.9	35.9
14.2	32.4	32.8
28.3	29.7	29.8
42.5	27.6	26.9
54.5	26.0	26.0

TABLE XII

$NaNO_3$ at 20°

x = g. $NaNO_3$ y = g. NaCl

$(x + 50)^{1.3}(y + 60) = C_1$

$\log C_1 = 4.558.$

y	x calc.	x obs.
0.0	87.6	87.6
6.5	77.0	77.3
13.0	68.3	68.5
19.5	60.8	60.5
26.0	54.4	54.5

TABLE XIII

NaCl at 20°

x = g. NaCl y = g. KCl

$(x + 18)^{2.4}(y + 50) = C_1$

$\log C_1 = 5.855$

y	x calc.	x obs.
0.0	35.9	35.9
4.1	34.2	34.4
8.3	32.6	32.7
12.4	31.2	31.3
14.0	30.7	30.7

Table XIV

KCl at 20°
x = g. NaCl y = g. KCl
$(x + 18)(y + 50)^4 = C_2$
$\log C_2 = 12.970$

x	y calc.	y obs.
0.0	34.8	34.5
6.5	28.6	29.7
13.0	24.1	24.7
19.5	20.6	20.4
30.7	16.1	14.0

In these tables and all that follow, the values x and y represent the weight of salt found in 100 grams of water rather than in one gram as previously. Where the temperature was lower than 30° or 40° a reduction was made in the value of A as nearly as possible corresponding to the change observed in passing from 40° to 30°. As has been said, the values of A and B are obtained from the solubility of the single salts in alcohol or acetone except that their value is multiplied by one hundred in these last equations, for the amount of salt in one hundred grams of water instead of the amount in one gram is used. Table XIV is not very satisfactory.

In Tables XV and XVI I have calculated some of the work of Ditte[1] on the mutual solubility of bases and salts. The agreement between the calculated and the observed results is not very good; but wherever there is a very large discrepancy the points in question do not seem to lie on the empirical curve describing the solubility. The value of the constant B for potassium hydroxide is probably not very accurate, for it was not determined from any previous experiments, but was calculated from the two sets of measurements here given.

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[1] Ann. Chim. Phys. (7) **10**, 556 (1897).

TABLE XV

KCl at 18°

x = g. KOH y = g. KCl

$(x + 18)(y + 50)^{2.75} = C$

log C = 6.548.

x	y calc.	y obs.
1.8	31.2	30.3
2.3	30.4	28.9
6.9	24.7	24.7
9.7	21.9	22.1
15.0	17.4	17.5
21.6	13.1	12.3
25.2	11.1	10.8
34.1	7.1	7.1
34.6	6.9	6.8
45.9	3.0	3.0
52.7	1.1	2.2
53.6	0.8	2.0

TABLE XVI

KBr at 17°

x = g. KOH y = g. KBr

$(x + 32)(y + 50)^{1.45} = C.$

log C = 4.494

x	y calc.	y obs.
3.6	56.9	55.9
11.3	43.4	43.4
17.7	34.9	35.8
23.1	29.3	28.1
27.8	24.8	24.8
43.5	13.7	13.7
58.0	6.5	6.5

I have also found it possible to extend this equation to a slightly different case in which one of the salts is replaced by a gas viz. hydrochloric acid. Engel[1] gives data for the solubility of quite a

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[1] Ann. Chim. Phys. (6) 13, 370 (1889).

large number of chlorides in hydrochloric acid of different concentrations. These results can be represented by the same general equation which has been used in the previous tables. I have tabulated the results for barium chloride, potassium chloride and sodium chloride. The value of *A* for barium chloride was taken from the work of Bancroft, the value for potassium chloride from the work of Bathrick. The agreement between the calculated and the observed results is good. The variation in the case of barium chloride is somewhat larger than in the other two cases, as would be expected, for barium chloride crystallizes with water of crystallization, and would thus offer greater experimental difficulties.

Table XVII

NaCl at 0°

$x =$ g. HCl $y =$ g. NaCl

$(x + 40)(y + 50) = C$

$\log C = 2.537$

x	y calc.	y obs.
0.00	36.1	36.1
0.41	35.3	35.3
0.74	34.5	34.3
2.08	31.8	31.7
3.79	28.7	28.8
6.14	24.7	24.8
12.60	15.5	15.5
23.37	3.5	3.9

We have thus found the value of *A* for any particular salt to be constant under quite varying conditions. The same value for *A* may be used whether the salt be precipitated by alcohol, acetone, or by a base, an acid or another salt having a common ion. These experiments, however, serve to illustrate the fact that the value of A can be determined with accuracy only by making very accurate solubility determinations.

The objection might be raised that almost any formula, containing as many arbitrary constants as these do, could be made to correspond with the experimental facts. This may be partly true in any particular case, e. g. five constants are used in the equations representing the solubility of sodium chloride in aqueous acetone and there are only about eleven values given. It is true even here, however, that if the value of *A* is varied much, the equation represents the facts with much less accuracy. If the constant *A* for potassium chloride is similarly determined, we may use these two constants in the equation describing the precipitation of sodium chloride by potassium chloride, then having but two arbitrary constants. In such a case we seldom have more than four or five measurements, so that it might be claimed that the two constants were sufficient. However, the same value of *A* may be used in the equations representing the precipitation of potassium chloride by potassium hydroxide or hydrochloric acid, and in these cases we have a rather large number of measurements made, over a considerable range of concentrations, and but two arbitrary constants are used.

TABLE XVIII

KCl at 0°

$x = g.\ HCl \quad y = g.\ KCl$

$(x + 12)(y + 50)^{2.6} = C$

$\log C = 6.006$

x	y calc.	y obs.
0.0	28.5	28.5
1.6	24.9	24.9
2.6	22.8	22.7
2.8	22.4	22.4
4.4	19.6	19.3
9.2	13.1	13.1
13.7	8.6	8.2
16.6	6.2	6.2

It seems therefore as if these formulae would not always remain empirical, when we consider the relation that exists between them. It is, however, true that a very considerable variation is possible in the constants employed, if too great accuracy is not required. We cannot then determine these constants satisfactorily, nor be sure that they apply absolutely to the results obtained by experiment, till more accurate work is done on the solubility of mixed salts, bases or acids having a common ion. When a large amount of accurate data has been compiled, we shall then be able to test these equations and determine whether they really do describe the facts determined by experiment. If further work does show that these formulae are correct, then it may be possible later to derive the constants which are now only empirical.

TABLE XIX

$BaCl_2$ at 0°

$x = $ g. HCl $\quad y = $ g. $BaCl_2$

$$(x + 15)(y + 50)^{1.4} = C$$

$$\log C = 3.852$$

x	y calc.	y obs.
0.0	31.5	31.6
0.4	30.1	30.5
1.1	27.5	28.6
1.9	24.9	25.6
5.5	15.2	15.4
7.3	11.4	11.2
8.8	8.6	7.3
12.5	2.9	3.0

In an aqueous solution, when a salt is precipitated by another salt having a common ion, two equations are required to describe the phenomena, according as one salt or the other is precipitated; and we have two curves, along one curve the one salt is precipitated, and along the other curve the other salt. When a salt is precipitated by some liquid consolute with water, two equations are also required, and this is explained by a change in the solvent, thus furnishing a point toward distinguishing between the solvent and the solute When a salt is precipitated by a base or an acid we find but one equation is required. This is as would be expected, as long as the base or the acid is not precipitated. However, we might also expect theoretically to obtain another curve, and that hydrochloric acid gas would be driven from a concentrated solution of hydrochloric acid by means of sodium chloride according to another formula. This would occur in the solution which separates as a second liquid phase. It must be remembered that the addition of sodium chloride always increases the partial pressure of hydrochloric acid in the vapor phase.

The results of this paper have then simply served to strengthen the points already brought out:

1. The behavior of ternary mixtures of the type here mentioned can be described by equations of the general form $(x + A)y^n = C$ and $(x + A)(y + B)^n = C$;
2. The constant n is independent of the temperature but varies with the precipitating agent;
3. A and B vary with the temperature and are each characteristic of one of the non-miscible substances, A being a function of y, and B of x.

Cornell University

NEW BOOKS

L'Entropie, sa Mesure et ses Variations. *G. Mouret. 93 pages. G. Carré; Paris.* Mr Mouret's little book is a somewhat diffuse essay, devoting over ninety pages to the wholly general features of the entropy function. In his introduction the author complains that the entropy is not, as a rule, accorded the position which it deserves, but is regarded usually as a purely mathematical function «destitute of all physical signification», wherefore he proposes to make clear that it really has the character of a «concrete physical quantity». Incidentally he expresses a conviction that the period of induction in the science of heat is now terminated, and a preference for deductive treatment of the entropy law, as against the «confused mixture» of the actual historical path. The special part of the book presents four «fundamental laws»: of equilibrium, of conduction, of reversibility and of irreversibility; a definition of entropy, as «the quantity defined by the reversible measure of isothermal transformations»; a consideration of absolute temperature, and of the increase of entropy in spontaneous changes; and, finally, a reference to the part played by the entropy in the course of organic evolution. The treatment dispenses almost entirely with the use of mathematical analysis.

J. E. Trevor

Physikalisches Praktikum. *E. Wiedemann and H. Ebert. Octavo. xxvi and 490 pages. Third Edition. F. Vieweg und Sohn; Braunschweig, 1897. Price 9 marks.* As stated in the preface this volume is intended for beginners and for students of chemistry. It is to be hoped that the time will come when a knowledge of the ground covered therein will be an essential part of a chemist's equipment. We have not yet reached that stage in this country; but we shall. The book is divided into four parts: general physics, heat, optics and electricity. The student first learns to make measurements of lengths and angles; acceleration is illustrated by the pendulum and by Atwood's machine; the use of the balance comes next and is followed by density determinations with solids and liquids. Experiments on gases, on elasticity, on viscosity, on surface tension and on acoustics round out the chapter entitled general physics. The exercises under the heading heat include, among other things, thermometry; freezing points and boiling points of pure liquids and of solutions; heats of reaction, using the term in the broadest sense. Under optics we have photometry; reflection and refraction of light; spectrum analysis and polarization phenomena. The chapter on electricity is the most interesting to the chemist and is very complete though the reviewer misses experiments on the transference numbers. There is appended to the volume a table of logarithms.

The book is very satisfactory and deserves wide spread recognition. The fact that the first edition appeared in 1890 and the third in 1897 shows that the merits of the volume have been perceived in Germany at any rate. *Wilder D. Bancroft*

Le Nickel. *H. Moissan et L. Ouvrard. In the Encyclopédie des Aide-Mémoire. Gauthier Villars et Fils; Paris.* This work treats of the physical and chemical properties of nickel, its compounds, the minerals in which it occurs, together with the methods for separating it from its various alloys, nickel plating, and the principal applications of the metal.

Among the compounds described is the interesting substance, nickel tetracarbonyl $Ni(CO)_4$, which is now used in preparing the metal in pure condition. The method of extracting nickel from its ore depends upon the composition of the mineral. If it contains arsenic, a different process is used from that employed when the mineral is a sulfid or oxid. The more important alloys of nickel are those with iron and copper. Nickel-steel finds considerable application. Nickel and copper alloy in all proportions and give valuable products. The applications of nickel in the preparation of wire, crucibles, *etc.*, are briefly considered.

The book ends with a bibliography of the subject treated.

Harry C. Jones

REVIEWS

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

General

The Genesis of the Atomic Theory. *H. E. Roscoe and A. Harden. Zeit. Phys. Chem.* **22**, *241; Phil. Mag.* [*5*] **43**, *153* (*1897*). Reply to Debus, this Journal, **1**, 187 (1896). Both parties to the controversy agree on what must seem to many to be the most important point, viz:—that Dalton's atomic theory was suggested by physical experiments with gases, and not by the results of chemical analyses. They differ with regard to Dalton's attitude to the ‹law of constant volumes› (Avogadro's hypothesis); Debus seeking to show that Dalton held to the hypothesis from 1801 to 1805, while Roscoe and Harden maintain that Dalton never definitively accepted it.

Debus's views were first made known in his pamphlet *Einige Fundamentalsätze der Chemie* (1894); and it can hardly be considered surprising that the subsequent discovery and publication (1896) of Dalton's laboratory note books—including a list of atomic weights *and sizes*, dated 1803—should necessitate a revision of conclusions arrived at without this important evidence. *W. L. M.*

Attempt at a Graphic Representation of the Periodic System of the Elements. *E. Loew. Zeit. phys. Chem.* **23**, *1* (*1897*). The paper begins with a diagram in which the symbols of the elements are arranged in the form of an Archimedean spiral; each element being represented by a point whose polar angle (in radians) is numerically equal to the square root of the atomic weight. The author points out that points representing members of a natural family lie—very roughly—in the same straight line; and then proceeds to compare the ‹traditional› atomic weights with ‹theoretical› values obtained by distributing the elements symmetrically over the spiral, with a constant difference of $\pi/16$ between the polar angle of each point and that of its next neighbors.

Expressed in another form, the author's hypotheses are equivalent to assuming that the atomic weights of the elements $(O = 16)$ are equal to the squares of members of the series $\pi/16$, $2\pi/16$, $3\pi/16$, *etc.* and that the differences between the square roots of the atomic weights of successive members of a natural family are numerically equal to π. $(\pi = 3.1416)$.

The author is careful to point out that his ‹theoretical› atomic weights are merely a very rough approximation to the true values,—silver, for instance, calc. 119, found 108—but with the hopefulness characteristic of workers in this ‹field›, he is convinced that «the method of approximation adopted is not altogether without promise».

W. L. M.

Heat of Dissociation of the Molecules of the Elements. *W. Vaubel. Jour. Prakt. Chem.* **55**, *542* *(1897)*. «I have succeeded in calculating the quantity of heat necessary to decompose one molecule Hg_2 (sic !) into its atoms. We have the equations

$$\begin{array}{l} 2Hg_2 + O_2 = 2Hg_2O + 640\ \mathrm{K} \\ Hg_2 + O_2 = 2HgO + 412\ \mathrm{K} \\ \hline \textit{Difference} \qquad\qquad 72\ \mathrm{K} \end{array}$$

The difference gives the quantity of heat set free when one molecule of the metal is decomposed into its atoms . . . under the assumption that the quantitity of heat liberated by the formation of HgO is the same as that liberated on the formation of Hg_2O»—an assumption with as little foundation as the other, viz. that the mercury molecule consists of two atoms ! *W. L. M.*

On the Atomic Weight of Cerium. *Wyrouboff and A. Verneuil. Comptes rendus*, **124**, *1300* *(1897)*. Starting with specially pure cerium and changing the hydrated sulfate $Ce(SO_4)_2 8H_2O$ into the oxid the authors obtain 92.8 for the combining weight of cerium.

W. D. B.

Description of an Open Manometer of 300 Meters in the Eiffel Tower. *L. Cailletet. Zeit. comp. Gase,* **1**, *88 (1897).* The instrument is a steel tube with 4.5 mm bore and giving a maximum mercury pressure of 400 atm. Its mercury is raised from a reservoir at the bottom, through displacement by water from a hydraulic pump, and the height of the column is read from the top surface in one of a series of side manometers of glass mounted three meters apart. The article gives a description of the corrections to be applied to the measurements; the apparatus has been used with complete satisfaction for over two years. *J. E. T.*

Long Range Temperature and Pressure Variables in Physics. *C. Barus. Science,* **6**, *338 (1897).* In this address, delivered at the Detroit meeting of the A.A.A.S., the methods of pyrometry and of piezometry are treated historically, critically and prophetically in a clear and very fascinating manner. The position of the author in these subjects is well known to be that of a first class authority.

J. E. T.

Thermal Phenomena Accompanying the Change in Rotatory Power of freshly prepared Solutions of Certain Carbohydrates. *H. T. Brown and S. U. Pickering. Jour. Chem. Soc.* **71**, *756 (1897).* The rotatory power of freshly prepared solutions of dextrose is diminished by half on standing. Addition of a small quantity of an alkali greatly accelerates the change and renders the reaction accessible to the methods of calorimetry. The authors find that the diminution in rotatory power is accompanied by an evolution of 0.588 cal per gram of dextrose. Similar experiments were made with maltose (no evolution of heat), laevulose (5 cal per gram absorbed) and milk sugar (0.2 cal evolved).

The paper contains a review of the various theories heretofore advanced to account for the phenomena of multirotation. *W. L. M.*

The Thermochemistry of Carbohydrate Hydrolysis. *H. T. Brown and S. U. Pickering. Jour. Chem. Soc.* **71**, *783 (1897).* Direct calorimetric measurements of the heat evolved on hydrolysis of starch by vegetable and animal diastase and that of sugar by invertase. The enzyme solution was placed in a pipette with suitably bent tube and immersed in the starch solution in the calorimeter.

When the temperature of the enzyme had become equal to that of the solution the contents of the pipette were forced out by means of a pump, and then some of the mixture in the calorimeter drawn in and forced out again in order to wash the pipette out. Check experiments showed that the method was capable of great accuracy.

The mean of six determinations shows that the heat evolved on hydrolysis of starch solution by pancreatin is about 30 percent greater than when malt extract is used; this difference is very remarkable, for the amounts of enzyme employed were extremely small in comparison with those of the starch: the most plausible explanation seems to be that the products of hydrolysis are different in the two cases. *W. L. M.*

On the Experimental Determination of the Hydrothermal Value of a Bomb Calorimeter. *H. W. Wiley and W. D. Bigelow. Jour. Am. Chem. Soc.* **19**, *139, (1897).* Description of the method of mixtures, using two Beckmann thermometers and two masses of water whose temperatures differ but little more than 10°C. *J. E. T.*

Monovariant Systems

On Lithium Borate. *H. Le Chatelier. Comptes rendus*, **124**, *1091; Bull. Soc. Chim. Paris*, **17**, *585 (1897).* Lithium borate, $LiH_2BO_3 7H_2O$, melts at 47°. Ice separates from the saturated solution at —0.6°. The solubility curve has been followed beyond the melting point to 37° at which temperature a new phase is formed, the nature of which was not determined. The author admits the existence of a vertical tangent at the melting point. *W. D. B.*

Experimental Verification of van 't Hoff's Constant in very Dilute Solutions. *M. Wilderman. Jour. Chem. Soc.* **71**, *796 (1897).* Careful measurements of the freezing points of dilute aqueous solutions of seven organic substances. The experiments were so arranged that in some cases the temperature of convergence was *above* and in others *below* the freezing point; and the apparatus employed enabled the freezing temperature to be kept «constant within 1, 2, 3 ten-thousandths of a degree during 10, 15, and 20 minutes and longer».

The ‹van 't Hoff's constant› as determined from the latent heat of ice is 1.87; as calculated from the freezing point measurement under consideration, it varies from 1.80 to 1.90. As the depressions (measured with a 1/1000 deg. thermometer) were for the most part only a few hundredths of a degree, the agreement must be regarded as remarkably close. *W. L. M.*

Contribution to the History of the Iodids of Phosphorus. *A. Besson. Comptes rendus.* **124**, *1346* (*1897*). Very interesting though incomplete data on the melting points and boiling points of the various iodids of phosporus. *W. D. B.*

On a Compound of Silver Chlorid and Monomethylamin. *R. Jarry. Comptes rendus,* **124**, *963* (*1897*). Equilibrium pressures for $AgClCH_3NH_2$, AgCl, solution and vapor. *W. D. B.*

The Effect of High Temperature on the Sulfids of Copper, Bismuth, Silver, Tin, Nickel and Cobalt. *A. Mourlet. Comptes rendus,* **124**, *768* (*1897*). In the electric furnace CuS changes to Cu_2S and then to metallic copper; bismuth sulfid changes to bismuth and silver sulfid to silver. On the other hand the sulfids of tin and nickel remain unchanged except that NiS passes to Ni_2S. *W. D. B.*

On the Alloys of the Silver-Copper Group. *F. Osmond. Comptes rendus* **124**, *1094*, *1234* (*1897*). A microscopical study of the lowest melting alloy of silver and copper shows that it is not chemically homogeneous and that the compound Ag_3Cu_2 does not exist. It was also found that copper and silver are mutually soluble to the extent of about one percent in each case. *W. D. B.*

On the Constitution of Metallic Alloys. *G. Charpy. Comptes rendus,* **124**, *957* (*1897*). A statement that eutectic alloys are not compounds. It is also urged that the microscope has shown the existence of the compounds Cu_3Sn and Cu_2Sb. *W. D. B.*

Studies on the Formation and Inversion of Solids, I. *W. Ostwald. Ber. sächs. Ges. Wiss.* **1897**, *254*. Reviewed, **1**, 586, from Zeit. phys. Chem.

Cryoscopic Measurements. *F. Garelli. Rend. Accad. Lincei,* **5**, *138*. Reviewed, **1**, 439, from Ber. chem. Ges. Berlin.

Divariant Systems

When do Gases become Liquid? *M. Thiesen. Zeit. comp. Gase,* **1**, *86 (1897).* An arbitrary definition, to the effect that a fluid is liquid or gaseous according as its density is greater or less than the critical density. The reviewer would think it better to make such a distinction between liquid and vapor below the critical temperature, and to say that all fluids above their critical temperatures are gases (more or less highly compressed). All stable vapors are then liquefiable by isothermal compression, and all gases are not. *J. E. T.*

On Corresponding Temperatures at Equal Vapor Pressures, *Second Paper. J. A. Groshans. Wied. Ann.* **61**, *142 (1897).* In a previous paper, Wied. Ann. **60**, 169 (1897), the author seeks to support his «law of corresponding temperatures»

$$\frac{T_p}{T_p'} = \frac{T}{373}$$

(where T_p and T are the boiling points in absolute degrees of any given substance under the pressure p mm and 760 mm respectively; while T_p' and 373 are the corresponding data for water) by quoting from Auschütz the boiling points of twenty-four substances, under 12 mm and 760 mm pressure respectively. The agreement is fairly close, the two quotients (given in the fourth column of his table) showing a maximum difference of less than two percent. The effect on the reader is however apt to be a good deal modified by the author's *naive* confession that «the 24 substances in the table have been selected from the 245 studied by Anschütz *on the principle of the least* difference between the pairs of numbers in the fourth column».

In the present paper the history of the discovery of the «law» in question is disclosed. The ratio of the vapor densities of ether and water at their boiling points (760 mm) is 4.98; while the numbers of atoms (B) in the molecule of each, *viz.* 15 and 3, stand in almost the same ratio. If this relation be general, the values of TB/A, (A = mol. wt.) must be the same for all liquids. Tabulation of experimental results shows that this is far from being the case, and the author concludes that «all values for TB/A may be united in one single formula

$$T = \frac{A}{B} 27.801 \sqrt{x}$$

by means of which the general law of boiling points is expressed». As x may apparently have any value whatever,—examples are given where $x = 5, 5.25, 3.5, 0.04$, *etc.*—this last relation may be regarded as a truism. Finally—the discovery of the «law»—«our equation $T_p/T = T_p'/373$ is founded on the fact that A, B and x must be considered as unalterable quantities, and that consequently T_p/T_p' must remain the same for all pressures». *W. L. M.*

The Reaction between β-Naphtol and Picric Acid in Aqueous Solution. *B. Kuriloff. Zeit. phys. Chem.* **23**, *90*, (*1897*). If the solubility of β-naphtol in water at 12.5°C be represented by a (mols in 100 cc), and its solubility in water to which b mols of picric acid per 100 cc have been added be represented by c, the concentrations of the β-naphtol, naphtol picrate and free picric acid in the latter solution will be a, $c - a$, and $b - (c - a)$ respectively. If no account be taken of the degree of electrolytic dissociation of the picric acid, the condition of equilibrium becomes:—

$$c - a = ka(b - c + a).$$

Five solubility determinations were made, the amount of picric acid added varying from zero to 0.2 per 100 cc; the value of the constant k in the above equation fluctuated between 3000 and 4000. The author communicates measurements of the electric conductivity of solutions of picric acid and of β-naphtol picrate to justify his use of the simple form of Guldberg and Waage's equation given above. *W. L. M.*

Dalton's Law in Solutions. *M. Wildermann. Jour. Chem. Soc.* **71**, *743* (*1897*). «According to Dalton's law the total pressure of a gaseous mixture in a given space is equal to the sum of the partial pressures of the constituents. In a solution of two or more substances it means that the total osmotic pressure of the two or more dissolved substances is equal to the sum of the partial osmotic pressures of each of them (provided they do not act on each other chemically). From the connection between osmotic pressure and freezing point depression it follows that the total depression is equal to the sum of the partial depressions of each of the dissolved substances». . . . «Since van 't Hoff's law of molecular depressions holds good provided the solution is very dilute, it is obvious that Dalton's law can hold good only in very dilute solutions.»

The paper contains careful measurements of the freezing points of dilute aqueous solutions of four pairs of organic substances; the results agree very well with the requirements of the «law». *W. L. M.*

On the Solubility of Liquids. *A. Aignan. Comptes rendus*, **124**, *1013* (*1897*). The author assumes that Alexejew's method of determining the solubility of one liquid in another (by noting the temperature at which clouding occurs) involves the assumption that the solubilities in the two phases are reciprocal. He therefore proposes replacing an accurate method by one that is hopelessly inaccurate. *W. D. B.*

A Simple and Efficient Boiling-point Apparatus for Use with Low- and High-boiling Solvents. *H. C. Jones. Am. Chem. Jour.* **19**, *581* (*1897*). To prevent radiation and the return of the condensed solvent directly into the boiling liquid, the solution is divided into two parts by a platinum tube encircling the thermometer. Determinations are made to show the merits of the apparatus. The possibility of an error due to changes of concentration by distillation has been overlooked. *W. D. B.*

Observations on the Molecular Volumes at 0° of Some Crystallized Carbohydrates. *Pionchon. Comptes rendus*, **124**, *1523* (*1897*). The molecular volumes at 0° of xylose, glucose, laevulose, saccharose, lactose, melezitose and raffinose are almost identical with the volumes of the hydrogen and oxygen in these substances if measured as ice at the same temperature. *W. D. B.*

Action of Free Bases on Salts. *A. Colson. Comptes rendus*, **124**, *502* (*1897*). Equilibrium pressures are given for the system, ammonium chlorid, piperidin hydrochlorid, solution and vapor, the vapor being chiefly ammonia. When diisobutylamin is substituted for piperidin the dissociation pressures are much lower, 53 mm at 11° as against 760 mm at 0° in the other case. The two organic hydrochlorids can each take up a second reacting weight of hydrochloric acid with formation of a solid compound. *W. D. B.*

Apparatus for Determining Molecular Weight. *G. Guglielmo. Nuovo Cimento (4)* **5**, *311.* Reviewed, **1**, 511, from Rend. Accad. Lincei.

Polyvariant Systems

Action of Dilute Nitric Acid on the Nitrates in Presence of Ether. *Tanret. Comptes rendus,* **124**, *463 (1897).* Addition of nitrates to a mixture of ether, water and nitric acid causes more of the nitric acid to pass into the ether phase. This natural result is attributed by the author to the dissociation of acid nitrates. *W. D. B.*

On the Formation of Ammonium Cyanid. *D. Lance. Comptes rendus,* **124**, *819 (1897).* At 1100° ammonia acts on carbon with formation of ammonium cyanid. The yield is greater if the ammonia contains free nitrogen and hydrogen. *W. D. B.*

On the Chlorobromids of Tin. *A. Besson. Comptes rendus,* **124**, *683 (1897).* The three compounds $SnCl_3Br$, $SnCl_2Br_2$ and $SnClBr_3$ can be separated by fractional distillation and crystallization. *W. D. B.*

On the Sulfoantimonites of Silver. *Pouget. Comptes rendus,* **124**, *1518 (1897).* From a solution of K_3SbS_3 silver nitrate precipitates Ag_2KSbS_3 or Ag_3SbS_3 depending on the relative concentrations. The double salt is decomposed by water with precipitation of Ag_3SbS_3 and by alkaline sulfids with precipitation of silver sulfid. *W. D. B.*

On Double Salts of Mercuric Haloids. *T. Harth. Zeit. anorg. Chem.* **14**, *323 (1897).* From aqueous solutions containing equivalent quantities of mixed mercuric and potassium haloids, ether and benzene separate mercuric bromid alone from a mixture of bromid and chlorid; mercuric cyanid from mixtures of cyanid with chlorid, bromid or iodid and mercuric iodid from mixtures of iodid and chlorid or bromid. The author has also prepared some double salts of the form $HgX_2K_2Y_2$ in the usual unsatisfactory way—by evaporating on the water bath and then allowing the solution to crystallize as it cools. *W. D. B.*

The Formation of (Active) Oxygen in the Slow Oxidation of Triethyl Phosphin and Benzaldehyde. *W. P. Jorissen. Arch. néerl.* (*2*) **1**, *54* (*1897*). Reviewed in this Journal **1**, 513 (1897) from Zeit. phys. Chem. **22**, 34 (1897). *W. D. B.*

Osmotic Pressure

The Diffusion Constants of Certain Metals in Mercury. *G. Meyer. Wied. Ann.* **61**, *225* (*1897*). A glass tube with perforated bottom was partially filled with 0.1 percent zinc amalgam, the latter being prevented by its surface tension from falling through the perforations. The lower end of the tube so prepared was made the anode in a bath of zinc sulphate solution, and by means of an adjustable current, the lower surface of the column of amalgam was kept completely free from zinc.

The percentage of zinc in the upper surface, U, of the column was determined from time to time by measuring the E.M.F. of the combination

$$U | ZnSO_4 sol. | 0.1 \text{ pct } ZnHg$$

and from the rate at which the zinc left the upper surface, its diffusion constant in the amalgam was calculated.

The method is applicable only to such metals as are more electropositive than mercury; the diffusion constants for Zn, Cd and Pb as determined by the author are of the same order of magnitude as those for electrolytes in aqueous solution. *W. L. M.*

Determination of Osmotic Pressure from Measurements of the Vapor Pressure. *A. A. Noyes and C. G. Abbot. Zeit. phys. Chem.* **23**, *56* (*1897*). The authors start with a modification of the Arrhenius diagram in which the semipermeable wall is placed quite infinitely near the top of the column instead of at or below the free surface of the solvent. The advantage of this very ingenious arrangement is that the column is pure solvent instead of solution. As formula for the osmotic pressure they write $P = \frac{S_0}{M}\int_p^{p_0} v\,dp$ where P is the osmotic pressure, S_0 the density of the solvent and M its reacting weight. Measurements were made with naphthalene and azobenzene in ether at 12.9°. The ratio of P to concentration is more nearly constant when the concentration is expressed in reacting weights per liter than it is when reacting weights per kilogram of solvent or per kilogram of solution are taken as the unit. The reviewer is glad to see that some one has at last perceived the importance of measuring the change of vapor pressure at constant temperature. *W. D. B.*

Velocities

The Saponification of the Triglycerids. *A. C. Geitel. Jour. prakt. Chem.* **55**, *429* (*1897*). R. Löwenherz has determined the rate at which acetic acid is formed in a mixture of triacetin with decinormal hydrochloric acid, and has compared his results with the requirements of the kinetic equation for a bimolecular reaction. The author points out that it is only at the very beginning of the experiment that the formation of acid is due exclusively to the decomposition of the triglycerid, as the diglycerid formed, itself undergoes sponification, yielding acid and a monoglycerid, which in turn decomposes into acid and glycerol. There are thus three bimolecular reactions taking place simultaneously in the solution; the author develops the equations representing the rate of change in such a system as follows:—

Let e represent the initial concentration (mols per unit volume) of the triglycerid and w that of the water in a mixture of the two substances, while x, y and z are the number of mols (per unit volume) of mono, di, and tryglycerid respectively, *which have undergone saponification* at the expiration of t minutes. There remain, consequently, $e - z$ mols of the triglycerid, $z - y$ of diglycerid, $y - x$ of monoglycerid and $w - (x + y + z)$ of water; and the rate of saponification is fully determined by the three simultaneous differential equations

$$\left.\begin{aligned} dx/dt &= k_1(y - x)(w - x - y - z) \\ dy/dt &= k_2(z - y)(w - x - y - z) \\ dz/dt &= k_3(e - z)(w - x - y - z) \end{aligned}\right\} \qquad (A)$$

The general solution of these equations is not attempted; if however e be set equal to unity, and

$$k_1 = k_2 = k_3 \qquad (B)$$

(an assumption justified by reference to Menschutkin's work), the expressions for dz/dy and dz/dx (obtained from equations A by division), may be integrated, giving

$$\left.\begin{aligned} y &= z + (e - x)\log_e(e - z) \\ x &= z + (e - z)\log_e(e - z) - \frac{e - z}{z}\left(\log_e(e - z)\right)^2 \end{aligned}\right\} \qquad (C)$$

By means of equation C the author calculates a table for the values of x and y corresponding to eleven different values of z (between 0.1 and 1.0) and illustrates the application of his results by a detailed study of the saponification of trimargarin.

The effect on the value of y produced by dropping restriction B is next considered; then follows a review of the various theories of rancidity; and the paper closes with formulas (closely related to equations A) representing the rate of change and the condition of equilibrium in a mixture of glycerol and acid—owing to ignorance of the values of the constants involved no comparison with experiment is at present possible.

This important paper, opening up as it does the subject of the chemical kinetics of simultaneous and connected reactions, may well serve as a model for the discussion of the rate of change in systems (such for instance as the reduction of bromic by hydriodic acid) which have hitherto defied calculation. *W. L. M.*

The Rate of Reactions in Solutions. *E. Cohen. Kon. Akad. Wetensch- Verslag. Amsterdam* **1897-98,** *49; in full Zeit. phys. Chem.* **23,** *442 (1897).* The rate at which sugar undergoes inversion in aqueous solution, at constant temperature, is usually said to be proportional to the *concentration* of the sugar in the solution; the word ‹concentration› being understood to mean the quantity of sugar in a fixed volume, *e.g.*, 100 cc, of the solution. A mathematical consequence of this assumption is the relation:

$$k = \frac{V}{t}\log_e\frac{A}{A - x}$$

(A the quantity of sugar initially present in the constant volume, $V = 100$ cc and x the quantity inverted at time t; k a constant).

Experiments carried out by Ostwald in 1885 show that the value of k is not independent of the initial concentration, A/V. The author of the present paper consequently proposes to modify the relation just quoted by replacing V by $V-b$, where b is interpreted as that part of the volume of the solution occupied by the sugar; and shows that the equation in its new form gives an excellent account both of the older data and of new experiments undertaken with a view of testing its validity. The change necessitates a corresponding alteration in the definition of the word ‹concentration›.

For 100 cc of 20 percent sugar solution at ordinary temperatures $b = 17.7$ cc; and for other concentrations it changes proportionately to the percentage of sugar. *W. L. M.*

On the Influence of Manganese upon Oxydations caused by Laccase. *G. Bertrand. Comptes rendus,* **124,** *1032, 1355 (1897).* Manganese salts act as catalytic agents increasing the oxidizing power of the soluble ferment of the lacquer tree. It was also found that these salts make free oxygen more effective. *W. D. B.*

On the Process of Oxidation and Chlorination. *A. Villiers. Comptes rendus,* **124,** *1349 (1897).* A reference is made to the catalytic action of salts of manganese which is attributed to the formation and decomposition of instable compounds. *W. D. B.*

The Rôle of Manganese in Certain Oxidations. *A. Livache. Comptes rendus,* **124,** *1520 (1897).* A statement that the author had chronicled in 1883 experiments similar to those of Villiers and of Bertrand, preceding two reviews. *W. D. B.*

The Rôle of the Peroxids in the Phenomena of Slow Oxidation. *A. Bach. Comptes rendus,* **124,** *951, (1897).* The author states that ‹active› oxygen is formed in many case of slow oxidation; but seems not to have heard of the work of van 't Hoff. *W. D. B.*

Action of Light on Mixtures of Chlorin and Hydrogen. *A. Gautier and H. Hélier. Comptes rendus,* **124,** *1128, 1267 (1897).* In the dark, chlorin and hydrogen do not combine to a measurable extent in fifteen months, whether moist or dry. When exposed to sunlight the reaction runs to an end, slowly with dried gases, rapidly when water is present. Excess of hydrogen or of chlorin increases the reaction velocity, the effect of the latter being the more marked. *W. D. B.*

Discussion of Reactions in Gases. *M. Berthelot. Comptes rendus*, **124**, *1273* ; **Reply.** *A. Gautier. Ibid.* **124**, *1276* (*1897*). Berthelot recalls the fact that the nature of the enclosing surfaces has a great influence upon reactions in gases, and questions whether the limited reaction between hydrogen and oxygen noted by Hélier, this Journal **1**, 604 (1897), may not be due to the action of the walls bringing in a case of heterogeneous equilibrium. To this Gautier replies that there can hardly be any effect due to the action of water on the walls unless hydrogen and oxygen do combine at 200°.

It is interesting to note the difference between the objections urged in France and those which would be urged in Germany. In Paris Gautier's statement that hydrogen and oxygen combine at 200° is questioned. In Leipzig he would be asked to prove that the reaction did not run to an end. *W. D. B.*

On the Explosive Properties of Acetylene. *M. Berthelot and Vieille. Comptes rendus*, **124**, *988, 996, 1000* (*1897*). In the first paper it is shown that acetylene dissolved in acetone explodes much less readily than when pure. In the second paper it is explained that this is in accord with the thermochemical data, while the third paper contains data proving that pure acetylene can be exploded much more readily by fulminate of mercury than by an incandescent wire.

W. D. B.

Rate of Crystallization. *G. Tammann. Zeit. phys. Chem.* **23**, *326* (*1897*). Reviewed, **1**, 613, from an undated reprint.

Electrolysis and Electrolytic Dissociation

On the Electrolytic Dissociation of Methyl Alcohol and of Water dissolved in it. *G. Carrara. Gazz. chim. Ital.* **27**, *I, 422* (*1897*). Pure methyl alcohol seems to be somewhat dissociated into the ions CH_3O and H. The amount dissociated is about six times that for pure water, comparing equal volumes. Addition of benzene decreases the conductivity. Addition of water increases it, possibly owing to the condutivity of the water. Assuming this to be the case the author shows that the dissociation of water is greater in methyl alcohol than in water alone. For dilute solutions the change in the dissociation of water dissolved in methyl alcohol varies with changing concentration according to the dilution law. *W. D. B.*

Electrolysis of Trichloracetic Acid. *K. Elbs and K. Kratz. Jour. prakt. Chem.* **55**, *502* (*1897*). When the sodium, zinc, or potassium salt of trichloracetic acid is subjected to electrolysis, no hexachlorethane is formed; but, instead, trichlormethyl-trichloracetate. The paper describes the conditions under which the best yield (10–30 percent of the theory) may be obtained. *W. L. M.*

On the Pressure Coefficient of Mercury Resistance. *A. de F. Palmer Jr. Am. Jour. Sci.* [*4*] **4**, *1* (*1897*). From measurements of electrical resistance at 9° and at 100°, the increase of resistance per atmosphere is found to be $-0.0000332 - 5 \times 10^{-9} t$. Barus (1890) had found -0.00003 for commercial mercury. *J. E. T.*

Structure Phenomena

Studies on the Coloring of Glass by Direct Penetration of Metals or Metallic Salts. *L. Lémal. Comptes rendus*, **124**, *1097* (*1897*). If glass be heated with a silver salt, it becomes colored yellow by cementation. Very interesting effects are obtained by adding traces of copper. *W. D. B.*

Two Methods of Measuring Dielectric Constants and Electric Absorption. *P. Drude. Zeit. phys Chem.* **23**, *267* (*1897*). The paper opens with a detailed account of the author's methods, illustrated by drawings of the necessary apparatus; and contains moreover a tabulated collection of the measurements so far made, and a restatement of the generalizations deduced from them, see this Journal **1**, 454 and 469, together with some new matter, principally with regard to the behavior of solutions. In general, the dielectric constant of a mixture can not be calculated from those of its components by means of the «mixture rule»; on the other hand the author finds no confirmation whatever of Thwing's alleged discovery of sharp angles in the curves having for their axes dielectric constants, and percentage composition of solutions. *W. L. M.*

Measurement of the Dielectric Constant, etc. *P. Drude. Wied. Ann.* **61**, *466* (*1897*). Reviewed **1**, 532, from Ber. sächs. Ges. Wiss.

Modern Criticism of the Methods of Determining Capillarity Constants. *G. Quincke. Wied. Ann.* **61**, *267* (*1897*). Polemic against Volkmann, Lohnstein and Sieg, in which the author repels their suggestions that his methods and instruments are inaccurate, and his mode of calculation faulty.

« Whether this be agreed to or not, the difficulty remains that determinations of the surface tensions of mercury and of water, made by different observers and by different methods, though carried out with all possible care, *give different results*—and that we can not account for these differences ». *W. L. M.*

Surface Tension of Water and of Dilute Aqueous Solutions. *N. E. Dorsey. Chem. News,* **76**, *22* (*1897*). The author has perfected Rayleigh's method of measuring surface tension by determining the wave lengths under known number of vibrations per second. The values tabulated agree well with those found by other methods. *W. D. B.*

Capillarity of Molten Metals. *H. Siedentopf. Wied. Ann.* **61**, *235* (*1897*). Reviewed, **1**, 532, from Gött. Nachrichten.

Theoretical Studies concerning Elastic Bodies and Light. *P. Glan. Wied. Ann.* **55**, *302* (*1895*), *to* **60**, *564* (*1897*). A long series of papers on the effect of the thermal conductivity of bodies upon their absorption of elastic waves. The comparison with observed facts leaves something to be desired. Compare the following review. *J. E. T.*

Absorption of Sound and Conductivity for Heat. *B. Brunhes. Jour. de Phys.* (*3*) **6**, *289* (*1897*). Incited by Glan's attempt—in a long series of papers in Wied. Ann.—to connect absorption of light with conductivity for heat, the author establishes a similar relation for the absorption of sound in a fluid, taking care not to neglect the specific heat at constant volume as against that at constant pressure, as was done by Glan. He finds for air the coefficient of absorption to be proportional to the square of the pitch, and negligible save for high pitches, which accords qualitatively although not quantitatively with the observations of Violle and Vautier. Further causes of absorption doubtless exist. *J. E. T.*

Absorption of Ultraviolet Rays by Vapors and Liquids. *J. Pauer. Wied. Ann.* **61,** *363* (*1897*). The measurements (with thirteen benzene derivatives, pyridin, thiophene and carbon disulfid) were made by the aid of a spectroscope with photographic attachment; light being supplied by a series of sparks between cadmium electrodes. The vapors, mixed with air, were contained in tubes, the liquids in troughs or as thin films between quartz plates.

With the exception of iodo- and nitro-benzene the spectra of the vapors consisted of individual lines or groups of lines; those of the liquids, of broad bands nearer the less refrangible end of the spectrum. The absorption in the case of benzene and its derivatives is remarkably great, corresponding in order of magnitude to that of the metals: a mere trace of the vapor of benzene in the air may be recognized by the appearance of four characteristic lines. *W. L. M.*

On Luminescence. *W. Arnold. Wied. Ann.* **61,** *314* (*1897*). A number of substances were subjected to the action of: *1*, Cathode rays; 2, Röntgen rays; 3, Becquerel's rays; 4, Goldstein's ‹canal rays›; 5, Hertz (discharge) rays: and the occurrence or non-occurrence of luminescence (photoluminescence, triboluminescence, thermoluminescence) was noted. So much difference was found between the actions of the various kinds of radiant energy, that the author feels assured of ultimately arriving at a method for analyzing a ‹light complex› by means of suitable fluorescent screens.

In connection with these experiments the behavior of a number of solid solutions (e. g. copper in calcium tungstate) was studied, and found to be quite different from that of a mere ‹mechanical mixture› of their components. *W. L. M.*

THE VAPOR-PRESSURE METHOD OF DETERMINING MOLECULAR WEIGHTS

W. R. ORNDORFF AND H. G. CARRELL

Preliminary Paper

An accurate and simple method for the determination of the vapor pressures of solutions at low temperatures would be of great value to the physical chemist not only on account of the great theoretical importance of these figures but also because the method could be used to determine the molecular weight of any dissolved substance. The simplest method of determining the vapor pressure of a solution in the laboratory is the one suggested by Ostwald and worked out to some extent by Walker[1] and later by Will and Bredig.[2]

Walker passed a current of air through three Liebig potash bulbs, two containing the solution and the third the solvent (water), and then through a U-tube containing pumice stone saturated with concentrated sulfuric acid. The loss of weight of the solvent bulb and the gain in weight of the U-tube, after the experiment had continued for twenty-four hours, furnished the necessary data for calculating the molecular lowering of the vapor pressure.

Will and Bredig substituted alcohol for water as it is a much better solvent for organic substances. They also determined the amount of the solvent evaporated by weighing the solution and solvent bulbs both before and after the experiment. Instead of using an aspirator and placing the bulbs in an air bath they forced the air through the bulbs, which were placed in a large water bath kept at a constant temperature by means of a thermoregulator and a mech-

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[1] Zeit. phys. Chem. **2**, 602 (1888).

[2] Ber. **22**, 1084 (1889).

anical stirring device. The loss of weight (s'), of the solution bulbs corresponds to the vapor pressure of that solution (p'), while the loss of weight, (s), of the bulbs containing the solvent corresponds in like manner to the difference in vapor pressure between the solvent and the solution, ($p - p'$). Substituting these values s and s' for $p - p'$ and p' it is very easy to calculate the molecular weight of the dissolved substance. In order to saturate the air completely with the alcohol vapor Will and Bredig used a modified Liebig potash apparatus with nine, instead of three, absorption bulbs. They passed the current of air through the apparatus generally for twenty-four hours at the rate of one liter per hour.

The work of Will and Bredig demonstrates clearly that the method is practicable and in the hands of careful workers can be made to yield good results. The present investigation was undertaken in the hope that it might be possible to simplify the method still further and reduce the time required for each determination and thus to make it a laboratory method for the determination of molecular weights of dissolved substances.

We used the method and apparatus described by Will and Bredig forcing the air through the bulbs instead of aspirating it as we found that by this method the air current was easier to regulate and gave a much more regular stream of air through the bulbs. As this regularity of the air current was a very important factor in the success of the method we also arranged the two carboys, used to give air under pressure, in such a manner that the air in the lower carboy was always under the same water pressure. In order to do this the siphon tube leading from the upper carboy was made to terminate in a U-tube just below the rubber cork in the lower carboy, while a tube open at both ends passed through the cork stopper below the surface of the water in the upper carboy. The pressure was thus kept constant being always equal to the pressure exerted by a column of water equal in height to the distance from the bottom of the open tube in the upper carboy to the top of the U-tube in the lower. This pressure could be varied by raising or lowering this open tube in the upper carboy and thus changing the distance between the ends of the two tubes. The U-tube in the lower carboy was so arranged that it touched the neck of the carboy and the water ran down the side of this receptacle instead of dropping to the bottom. This arrangement we found to work very satisfactorily and to give a very constant and regular current of air through the bulbs.

After the water in the upper carboy had flowed into the lower it was drawn back again by exhausting the air in the upper carboy by means of a Chapman water pump and at the same time connecting the lower end of the siphon tube with a rubber tube leading to the bottom of the lower carboy. The same water was thus used over and over again so that the air passed through the bulbs was always at the room temperature.

After much experimenting with various forms of absorption apparatus including Geissler potash bulbs, U-tubes filled with glass beads, Liebig potash bulbs, Winkler's spiral, Mitscherlich's tube improved by de Koninck and the modified form of the Liebig apparatus of Will and Bredig having nine instead of three absorption bulbs, we found that this apparatus of Will and Bredig gave the best results. We therefore used this apparatus in our work. In having the apparatus made, however, we had the tubes connecting the absorption bulbs, (the nine small bulbs at the bottom of the apparatus), as well as those leading to the bulbs made of very small diameter, so that the bubbles of air passing through these bulbs should be as small as possible and thus facilitate the saturation of the air with the vapor of the liquid. Of course in using this apparatus it was slanted in such a manner that the current of air had always to force its way through a current of the liquid flowing in the opposite direction.

At first we used a large water bath kept at a constant temperature by means of a thermoregulator and a mechanical stirrer kept in motion by means of a Raabe's turbine. The bulbs were fastened to a wire frame immersed in this bath and were connected in the bath with a lead coil of pipe ten feet in length, through which the air was passed in order that it might have the temperature of the bath before passing through the bulbs. The air was dried by passing it through two calcium chloride towers filled with dry, porous calcium chloride. By means of this water bath it was possible to keep the temperature constant within half of a degree for twenty-four hours and after the turbine was once set in motion the apparatus required no further attention. It was soon found, however, that the water in the bath became very dirty and that it was difficult to wash the absorption apparatus clean. Washing the apparatus with alcohol and then with ether and allowing to dry gave unsatisfactory results. For these reasons and in order to get rid, if possible, of this clumsy piece of water bath apparatus, which required constant attention to keep it in order, charging the water and regulating the stirrer, etc., we made several experiments without this bath, simply passing the air current through the bulbs left in the air. The temperature variation amounted to as much as 2 to 6 degrees at times but was generally not over 1 degree. The results obtained by this modification were fully as good as those obtained by Will and Bredig using their complicated water bath so that we at once discarded this part of their apparatus. In beginning the work we thought that the method might be improved by passing the air current through the solvent first and then through the solution under investigation. We thus thought to get rid of changes in concentration which are sometimes quite large when the air is first passed through the solution. We expected that the loss in weight of the solvent bulbs would be proportional to the vapor pressure of the solvent while the solution bulbs would gain in weight owing to the distillation of the solvent from the point of higher vapor pressure to that of the lower. This modification of the method, however, was found not to give satisfactory results, notwithstanding its promises and hence was abandoned. In order to get rid as far as possible of the influence of these changes in concentration in the solution bulbs we slanted the apparatus as much as possible thus preventing the passage of the solution from one set of the three bulbs to the other in the same piece of apparatus. In this way the evaporation of the solvent took place almost entirely in the first set of three bulbs in the modified form of the Liebig apparatus of Will and Bredig, while in the other two sets of bulbs only slight changes in concentration took place. The air passed through a solution of lower vapor pressure in the first set of bulbs to one of higher in the second and third and was thus gradually saturated up to the vapor pressure of the solution when it left the third set of bulbs. After one experiment was completed the solution in the three sets of bulbs was thoroughly mixed by drawing the liquid over into the large bulb and the apparatus was then ready for another experiment without recharging; for the loss in weight represented only loss of solvent and the new concentration of the solution was easily calculated from this loss. It was thus possible to make a series of four or five determinations with increasing concentrations exactly as is done in determining molecular weights by the boiling-point method. This makes the method more accurate and less troublesome than where single determinations are made as was done by Will and Bredig. In the preliminary work it was soon found that the solvent bulbs invariably lost more in weight than they should theoretically. It was thought that this might be due to the fact that the solvent evaporated directly into the air. We therefore tried connecting the solvent bulbs with a U-tube filled with glass beads and containing a small quantity of the solvent. This device we found to be of great value and made use of it in all of our experiments. This U-tube was not weighed but was merely used as a precautionary measure.

Notwithstanding that the bulbs were kept tightly closed with small rubber tubes plugged in the usual manner with pieces of glass rod we found that in twenty-four hours a loss of over 10 milligrams took place, so that it is advisable in working with this method to reduce the time of the experiment as much as possible. The rate at which the air is run through the bulbs is a very important factor in this method. With some substances like urethane good results may be obtained using almost any rate while generally there is one rate which gives the best results. In the table we give some results in which we used alcohol as a solvent. The alcohol was carefully purified by distillation over lime until it was free from water.

In calculating the molecular weight we used the formula

$$M = \frac{46\ g\,s'}{100\ s}$$

in which

M = the molecular weight of the dissolved substance
g = the number of grams of the substance in 100 of the solvent
s = the loss of weight of the solvent bulbs

s′ = the loss of weight of the solution bulbs

46 = the molecular weight of the alcohol used as a solvent.

Urethane,

$OC{NH_2 \atop OC_2H_5}$, 89

Concentration in 100 grams	Loss of wt. of solvent	Loss of wt. of solution	Mol. wt. found	Duration hours	No. of liters of air	Temp. variation
g	s	s′	M			
23.9452	0.3828	3.2502	94	7.5	30	1.5°
15.2312	0.1785	2.2418	88	5	23	2.3°
15.2312	0.1270	1.6864	93	4	20	3.4°
16.6506	0.0568	0.6876	93	6	13	0.7°
17.3083	0.0796	1.0342	103	3	13	0.8°
18.4017	0.1306	1.3752	89	5.75	13	1.1°
Diphenylamine, $(C_6H_5)_2NH$, 169						
7.9902	0.0150	0.6016	147	3.25	10	0.5°
8.3200	0.0494	2.0680	160	9.75	20	3.2°
Nitrobenzene, $C_6H_5NO_2$, 123						
7.1130	0.0310	1.2448	131	14	27	6.1°
7.5199	0.0589	2.0848	122	32	41	2.9°
8.3176	0.0949	2.7357	110	28	40	0.7°
α-Nitronaphthalene, $C_{10}H_7NO_2$, 173						
5.6775	0.0512	3.0108	154	54	40	5.2°
5.6775	0.0606	3.3700	145	43	40	3°
Phenol, C_6H_5OH, 94						
33.4394	0.9420	4.0622	66	23	40	1.1°
41.9522	0.6270	2.2726	70	57	34	1.8°
7.5355	0.1018	2.1422	73	55	23	1.7°
8.2204	0.0677	1.4204	79	15	16	1.9°
8.7473	0.1117	1.8484	67	17	17	1.6°

Urea, $OC(NH_2)_2$, 60

Concentration in 100 grams	Loss of wt. of solvent	Loss of wt. of solution	Mol. wt. found	Duration hours	No. of liters of air	Temp. variation
g	s	s′	m			
3.1641	0.0538	2.0171	55	19	25	1.1°
3.4539	0.0660	1.9260	46	25	18	0.9°
3.7854	0.0736	2.6354	62	25	26	2.°
3.1641	0.0648	2.2614	51	44	26	1.1°
3.4406	0.0670	2.9476	70	22	29	3.2°

It will be seen from this table that the rate at which the air current passes through the apparatus influences markedly the results. In some cases, however, results agreeing with the theoretical are obtained whatever be the rate as is seen in the case of urethane while with phenol the results do not agree very well with the theoretical whatever the rate. It is quite likely that some other factor comes in here, possibly that the surface tension of the solution plays an important part.

Further work will be undertaken in this laboratory with this method, using other solvents like acetone and chloroform.

Cornell University, July, 1897

TERNARY MIXTURES, III

BY WILDER D. BANCROFT

Some twenty years ago Duclaux[1] found that a clear solution composed of amyl alcohol, ethyl alcohol and water in certain definite proportions could be made to cloud and separate into two layers by the addition of a drop of amyl alcohol or of water. This result has been confirmed by all who have since then studied the behavior of two liquid phases containing three components and it may be stated as a general proposition that, with two partially miscible liquids and a third consolute with the other two, it is always possible to prepare a series of solutions any one of which will cloud on addition of a drop of either of the two partially miscible liquids. This means that if we construct an isotherm for such a system using a triangular diagram, there must be a portion of the curve from any point of which lines drawn to the corners for the two partially miscible liquids will pass at once into the field for two solution phases. It is the object of this paper to show that one can deduce from the triangular diagram certain phenomena which have already been found experimentally but which have seemed hitherto to be lacking in theoretical justification.

In Fig. 1 is given the general form of the isotherm for a system composed of two partially miscible liquids, A and C, and a third liquid, B, miscible in all proportions with the other two. The points x and x_1 give the compositions of the two liquid phases when only A and C are present. On adding the third liquid the phases vary in composition, the change in one being represented by the line xyz and the change in the other by the line x_1y_1z. At the point z the two solution phases become identical. The field for unsaturated

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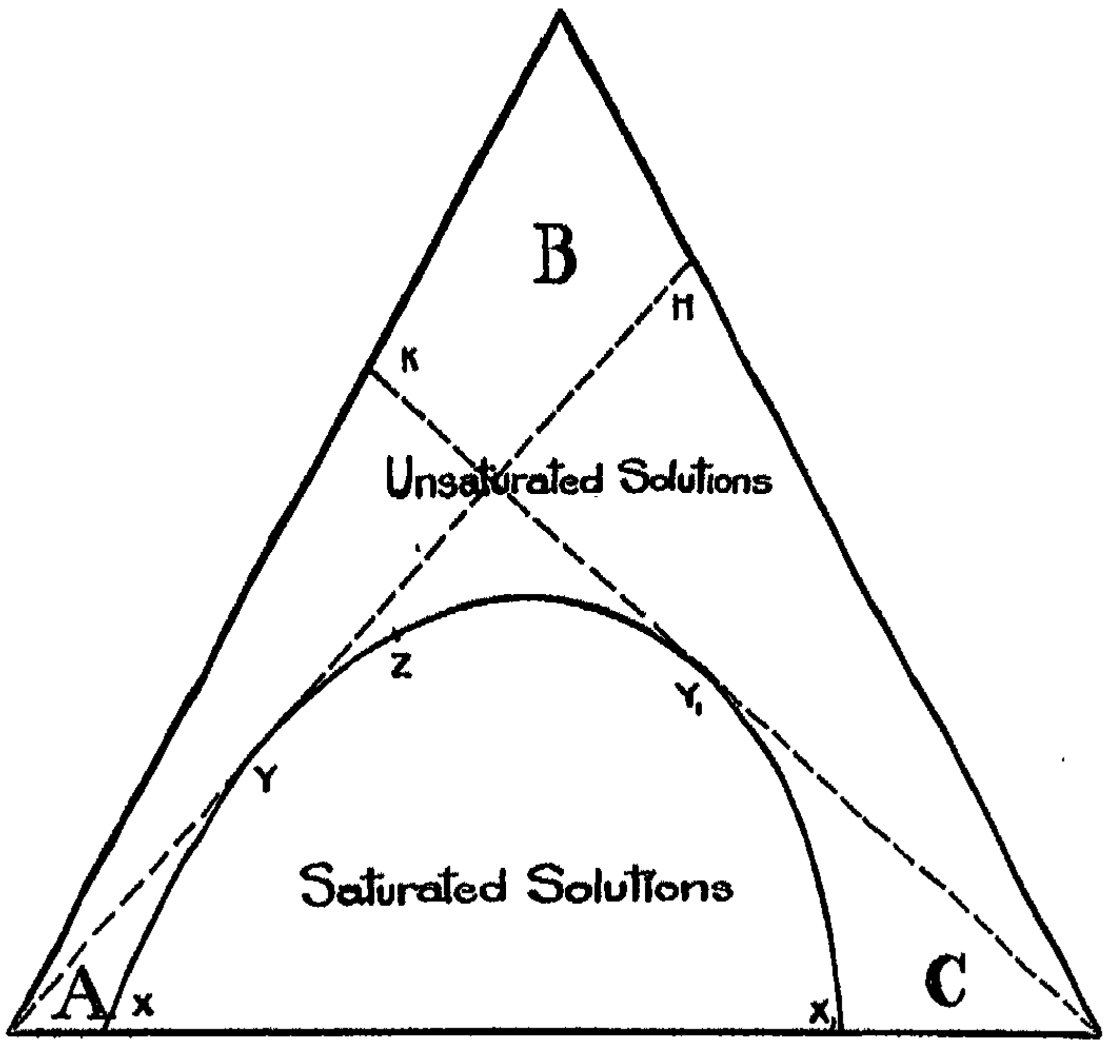
[1] Ann. Chim. Phys. (5) 7, 264 (1876).

solutions lies above and outside the isotherm while the field enclosed by the curves represents mixtures which separate into two liquid phases having compositions given by two points on the isotherm. From any point on the curve to the right of y and to the left of y_1 a straight line drawn either to the corner at A or to the corner at C passes into the field for two solutions immediately on leaving the isotherm. Addition of either A or C will therefore produce clouding and the isotherm as drawn is in accordance with the experimental data recorded by Duclaux. With the diagram before us it is possible to draw another conclusion not reached by Duclaux. At the point x it is clear that addition of C will cause clouding but that addition of A will not. There must therefore be some point between x and z beyond which addition of A will cause clouding. This will occur at the point at which a straight line through the corner at A becomes tangent to the curve. In the diagram this point is marked y and the intersection of the tangent with the side BC is represented



by H. If we start with a mixture of B and C containing less of B than the mixture denoted by H, addition of the liquid A will eventually cause clouding and formation of two liquid phases. If, however, we start with a mixture of B and C containing more of B than the solution denoted by H, addition of the liquid A will not cause clouding.[1] This phenomenon was first realized experimentally by Pfeiffer,[2] working in Ostwald's laboratory. Starting always with three cubic centimeters of a given ester he added varying quantities of alcohol and then saturated with water. On passing a given ratio of alcohol to ester—the value of the ratio being a function of the nature of the ester—he found that it was impossible to produce turbidity by addition of water. If we call water A, ester C and alcohol B, the critical concentration is evidently that of the point H. The same reasoning shows us that somewhere on the curve x_1z there must be a point at which a line through the corner at C is tangent to the isotherm. This point is represented in the diagram by y_1 and the intersection of the tangent with the side AB is denoted by K. It is clear that K and y_1 correspond to H and y.

The isotherm is thus divided into four parts by the three points y, z and y_1. Along xy addition of C produces cloudiness; addition of A does not. The precipitate formed by adding C will contain more of C than the original solution. Along yz addition of either A or C will produce cloudiness. The new liquid phase will contain more of A than the original solution. Along zy_1 addition of either A or C will cause precipitation. The second phase contains more of A than the first. Along y_1x_1 addition of C has no effect while addition of A causes clouding. The precipitate is chiefly A. Since these four portions of the isotherm are so distinct in their properties[3]

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[1] These peculiarities of the isotherm have already been pointed out by Schreinemakers, Zeit. phys. Chem. **23**, 652 (1897). In his paper he was considering qualitative equilibrium whereas I wish to bring out the bearing of these points upon the quantitative equilibrium.

[2] Zeit. phys. Chem. **9**, 469 (1892).

[3] Roozeboom and Schreinemakers have shown that when the part of the isotherm for a ternary compound, solution and vapor consists of a closed curve, it may be considered as divided into six portions, Zeit. phys. Chem. **15**, 611 (1894). They do not conclude from this that there are any points of discontinuity in the curve.

one would expect the compositions of each series of solutions to vary in general in slightly different ways. While studying systems of this type during the winter of 1893–94 I found that the experimental data for the whole isotherm could be represented by the same general formula :

$$\frac{(x - s_2 y)^n (y - s_1 x)}{z^{n+1}} = constant.$$

In this formula x, y and z denoted the amounts of the liquids A, C and B respectively in a constant quantity of the three. In the experiments as actually made these values were expressed in cubic centimeters; but it was shown at the time that any other units might have been taken without changing the general form of the equation. In the formula s_2 denotes the solubility of liquid A in liquid C while s_1 denotes the solubility of liquid C in liquid A. While the same general formula described the equilibrium along the whole isotherm, it was found experimentally that four values of the exponential factor and of the integration constant must be assumed in order to describe the facts accurately. At the time I pointed out that these four distinct sets of eqilibrium referred to the following four series of saturated solutions.[1]

1. The solution is saturated with respect to C. Excess of A produces no precipitate.

2. The solution is saturated with respect to C. Excess of A or C produces a precipitate of C.

3. The solution is saturated with respect to A. Excess of A or C produces a precipitate of A.

4. The solution is saturated with respect to A. Excess of C produces no precipitate.[2]

It will be noticed that the conditions for the four sets of equilibria as deduced from the experimental data are identical with those which can be predicted from the knowledge of the single fact that

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[1] Proc. Am. Acad. **30**, 340 (1894) ; Phys. Rev. **3**, 120 (1895).

[2] In the original B is used instead of C as I took A and B as the partially miscible liquids. It was also stated there that «precipitate of A» was used as a condensed phrase meaning that the new phase contained more of A than the old one.

there are some solutions which cloud on addition of either of the partially miscible liquids. We can see also from the diagram that the ratio of C to B passes through a minimum at y and the ratio of A to B passes through a minimum at y_1. If therefore we work with a constant quantity of B and varying quantities of A and C we should expect to find the amount of C decreasing as we pass from z to y and increasing as we pass along the curve from y to x. Similarly the amount of A in the saturated solution would decrease from z to y_1 and increase from y_1 to x_1. This is exactly what I found in the experimental studies already referred to.

If the liquids A and C are practically non-miscible the points x and x_1 will coincide very closely with the corners at A and C respectively. Other things being equal, the points y and y_1 will approach the corners A and C as the non-miscibility of the liquids increases and the curves xy and x_1y_1 will decrease in length.[1] With practically non-miscible liquids such as benzene and water, chloroform and water, these two curves will not be realizable experimentally unless one works on a colossal scale and we should therefore expect to find but two sets of equilibria. Two conclusions which I drew from the experimental data which were tabulated in my first paper on ternary mixtures were:[2]

1. For two partially miscible liquids and a consolute liquid there are four sets of equilibria corresponding to four different series of solutions.

2. If the two liquids are practically non-miscible, there are only two sets of equilibria.

It is, of course, not necessary that there should be any points of discontinuity in the isotherm. It is always conceivable that the same expression might describe the whole curve. With benzene, alcohol and water there seems to be no break at the point z. What can be stated definitely is that if there are points of discontinuity they can occur only at y, z and y_1. The fact that breaks at y and y_1 have been found in all cases that have yet been studied and that

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[1] The positions of y and y_1 will vary with the nature of the consolute liquid unless A and C are absolutely non-miscible.

[2] Proc. Am. Acad. **30**, 368 (1894); Phys. Rev. **3**, 204 (1895).

only one case is yet known in which there is not a break at z together with the fact that no breaks in the curve have been found at any other points is strong evidence that y, y_1 and z are theoretically points of discontinuity. This becomes the more probable when one recalls that these points were determined experimentally long before their theoretical significance was perceived.

Cornell University

MOLECULAR WEIGHTS OF SOME CARBON COMPOUNDS IN SOLUTION

BY CLARENCE L. SPEYERS

This paper gives some data concerning the molecular weights in solution of the same substances in the same solvents whose heats of solution were given some time ago.[1]

I wished to find the molecular weights at the ordinary temperature, 25°–35°. I tried the method of Walker[2] and that of Loeb[3] but could not get satisfactory results in either case.

The only method I found available was the boiling point method in a partial vacuum. Some of the results were so unexpected that I thought it best to make determinations at several temperatures intermediate between the boiling point under the atmospheric pressure and the boiling point under the lowest pressure obtainable by the water pump.

The apparatus was essentially that of Orndorff and Cameron.[4] As a partial vacuum of about 50 mm Hg was needed, mercury seals were used wherever the joints had to be broken in cleaning and charging the apparatus. Stationary joints could be made tight with rubber tubing and asphalt varnish. The boiling tube, *c*, held from the bottom up to *a* down to *g* about 350 cc. It was all in one piece. As recommended by Orndorff and Cameron a quantity of scrap platinum, about fifty grams, was used; no platinum wire was fused through the bottom at all. At the neck of the boiling tube is a mercury seal, the thermometer being held in place, of course, by cork or rubber. I could not detect a trace of injury.[5] At *a*, where

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[1] Jour. Am. Chem. Soc **18**, 146 (1896).

[2] Zeit. phys. Chem. **2**, 602 (1882).

[3] Zeit. phys. Chem. **2**, 606 (1882).

[4] Am. Chem. Jour. **17**, 517 (1895).

[5] Cf. Fuchs. Zeit. phys. Chem. **22**, 72 (1897).

connection is made with the water pump, a rubber cork and mercury seal are used. The pump gave a partial vacuum of about 44 mm. The tube, *e*, contained the substance to be introduced into *c* in the form of small weighed pellets. They were successively pushed in by a small glass pusher, *f*, which floated on mercury. The height of the mercury could be adjusted by raising or lowering *j*. To prevent air from entering through the rubber tubes, a trap, *h*, was used. The tube, *i*, with tap was convenient in letting out the trapped air. The connection between boiling tube and mercury was made at *g* by a thick rubber tube, sealed with mercury. A glass demijohn, 18 liters capacity, was circuited between the pump and *a*. Ice water circulated through the condenser *b*. When boiling under atmospheric pressure, the boiling tube was separated at *a* and *g* and used alone, the substance being introduced at *a*.

Under atmospheric pressure, the time used for solution was one and a half minutes or less, and the thermometer was so steady that no correction was needed.

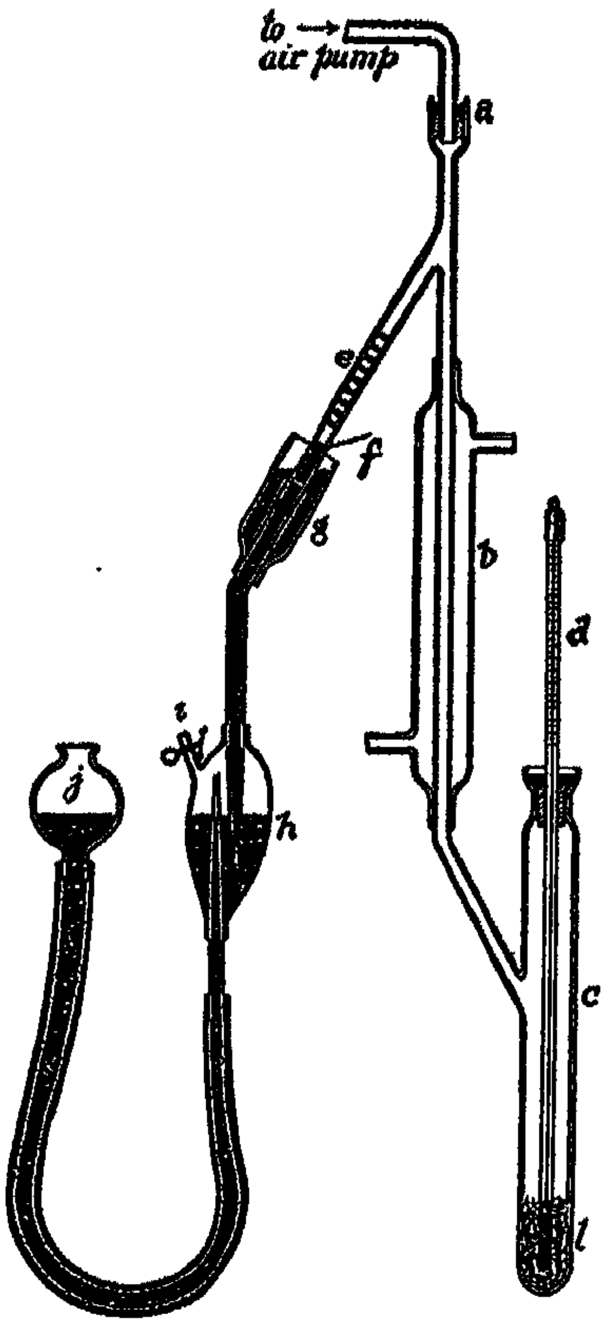

FIG. 1

Under less than atmospheric pressure, the boiling temperature was often so low that a considerable time was needed for solution and the thermometer was not so steady as it was under atmospheric pressure. A correction was therefore needed. It was computed in this way. The average change in the thermometer per minute for five minutes before solution and the average change per minute for five minutes after solution were added together, the sum divided by two, and this quotient multiplied by the number of minutes needed for solution. This, as a correction, was subtracted or added as the case might be, from the observed rise in the thermometer, to get the corrected rise. The thermometer was a Beckmann one divided into 1/100° and was estimated in reading to 1/1000°.

No corrections were made for the change in volume of the bulb of the thermometer due either to the temperature or to the pressure.

The gas was somewhat unsteady but did not give serious trouble. There was some difficulty once in a while with foaming which sometimes necessitated a lowering of the flame during a series of measurements, to prevent the solution from foaming out of the boiling tube and uncovering the bulb of the thermometer.

The correction due to the quantity of solvent which filled the boiling tube as vapor is easily calculated, at least approximately. But the quantity which trickled down the side of the boiling tube from the condenser can not be so calculated and the molecular weights are to this extent a trifle too low. This error is not more than one-half of one percent, if so much.

Experiments showed that no solvent passed the condenser tube.

The solutes and solvents have already been described.[1] When any substance gave out, some more was prepared according to the method previously used and identified by melting point or by boiling point.

The constant, K, for each solvent at the boiling point under atmospheric pressure was taken from Beckmann,[2] except for toluene. That solvent is not listed. How its constant was determined is described further on. The constants given by Beckmann are the mean of several different methods of determination and so it seemed better to use them than to determine the constants again. Under reduced pressure, they had to be determined in one of the following ways:—

1. Trouton's rule, $Q/T =$ constant, where Q is the molecular heat of vaporization and T is the absolute temperature of vaporisation, is not available for this purpose for the constant is different at different temperatures, even for the same substance, for as T falls,

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[1] Jour. Am. Chem. Soc. **18**, 146 (1896).

[2] Zeit. phys. Chem. **18**, 473 (1895).

Q rises, in so far as Q refers to heat needed for vaporisation, not the heat needed to dissociate complex molecules, Ramsay.[1]

2. If K_0 is the constant at T_0, and q_0 is the heat of vaporisation at T_0, then the constant K, at T, at which q_0 becomes q, is

$$K = K_0 \frac{0.02T^2}{T_0^2} \frac{q_0}{q}.$$

The chief objection to this formula is want of sufficient data for q. Only data for chloroform, methyl alcohol, and water, that were at all sufficient for the purpose, could be found. In the case of chloroform, the results were satisfactory but in the case of methyl alcohol and water, the results were suspicious. For instance, the following table gives the data for acetanilid in methyl alcohol. Weight of acetanilid $= w$, weight of solvent corrected $= W$, both in grams, rise in boiling point corrected $= \Delta t$, correction which has been made for Δt in percent of observed $\Delta t =$ cor., $K =$ constant from Beckmann (B) or calculated by the above equation. Assumed molecular weight $= M_0$, observed molecular weight $= M$.

Temp. = 66° W = 32.80
K(B) = 8.8 $M_0 = 135$

w	Δt	Cor.	M
0.672	0.133	0%	136
1.208	0.242	"	134
1.938	0.385	"	135
2.643	0.517	"	137
3.338	0.648	"	138
4.037	0.772	"	140

Temp. = 43.5° W = 34.55
K(B. calc.) = 7.37 $M_0 = 135$

w	Δt	Cor.	M
0.705	0.122	0%	123
1.290	0.225	"	122
1.929	0.325	"	127
2.621	0.434	"	129
3.284	0.532	"	132
3.947	0.627	"	134

Temp. = 25° W = 33.13
K(B. calc.) = 6.40 $M_0 = 135$

w	Δt	Cor.	M
0.490	0.084	2 %	113
0.888	0.153	0 "	112
1.300	0.231	3 "	108
1.735	0.299	3 "	112
2.111	0.368	3 "	111

The constant for the first case is taken directly from Beckmann and the somewhat high values are to be attributed to association of the solute.

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[1] Zeit. phys. Chem. **15**, 108 (1894).

In the second case, however, the constant seems to be too low and in the third case this is markedly so. In the second case the corrections are zero and the error in reading the thermometer at most two percent of the reading. In the third case, the corrections are three percent and the error in reading the thermometer at most three percent, making a maximum error of six percent which will not account for the low values of M. A similar drop in M as T decreases was found for most of the other substances in all the solvents.

3. Another method is to select a substance of constant molecular weight and deduce the constant from this.

The advantage of this method is that it seems applicable to all solvents at all temperatures, whereas the data needed for the other two methods are not known for all solvents. Besides, any uncertainty due to loss of solvent by vaporisation and loss by clinging to the sides of the boiling tube, and any uncertainty due to expansion of the bulb of the thermometer, all these are eliminated.

The disadvantage is the uncertainty as to whether the solute has the molecular weight in solution that it it is supposed to have. This uncertainty can be partly eliminated by selecting a solute whose molecular weight is the same at different dilutions. Then its molecular weight may be considered to be the simplest possible one, for complex molecules seem to decompose into simpler ones as dilution increases. But even in this case great discretion must be used.[1] Notwithstanding these disadvantages, this method was used whenever a solute could be found which seemed to have a constant normal molecular weight.

In the following table, K(B) means that the constant has been taken from Beckmann's tables; K(urea) means that the constant has been computed from experiments with the substance named in the brackets, in this case urea; K(calc.) means that the constant has been calculated by the furmula given on page 769. The necessary data for K were obtained from Landolt and Börnstein's tables unless otherwise stated. Under percent is given parts of solute in 100 parts of *solvent*. The other symbols have been defined

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[1] See table for urethane in water.

Water

Urea

Temp. 100° W = 44.19
K(B) = 5.1 M_0 = 60.

w	Δ*t*	Cor.	%	M
0.494	0.090	0%	1.1	63.6
0.985	0.176	"	2.2	64.9
1.485	0.269	"	3.4	63.9
1.885	0.342	"	4.3	63.9
2.276	0.414	"	5.1	63.7
2.746	0.496	"	6.2	64.1

Temp. = 75° W = 44.06
K(urea) = 4.32 M_0 = 60

w	Δ*t*	Cor.	%	M
0.978	0.159	0%	2.2	60.4
1.971	0.318	"	4.5	60.0
2.846	0.458	"	6.5	60.1
3.862	0.619	"	8.8	60.4
4.365	0.705	"	9.9	59.9

Temp. = 54.8° W = 44.22
K(urea) = 4.05 M_0 = 60

w	Δ*t*	Cor.	%	M
0.702	0.108	0%	1.6	59.6
1.446	0.221	"	3.3	60.0
2.172	0.330	"	4.9	60.3
2.928	0.446	"	6.6	60.2

Temp. = 35.5° W = 41.19
K(calc.) = 3.72[1] M_0 = 60

w	Δ*t*	Cor.	%	M
0.552	0.081	0%	1.3	62.5
1.229	0.189	"	2.9	58.1
1.606	0.261	"	3.8	54.4
1.915	0.317	"	4.5	53.3

Resorcinol

Temp. = 100° W = 44.86
K(B) = 5.1 M_0 = 110

w	Δ*t*	Cor.	%	M
0.854	0.090	0%	1.9	108
1.743	0.169	"	3.9	117
2.637	0.247	"	5.9	122
3.539	0.318	"	7.9	127

Temp. = 75° W = 40.59
K(urea) = 4.32 M_0 = 110

w	Δ*t*	Cor.	%	M
1.146	0.143	0%	2.8	85.4
2.575	0.264	"	6.3	104
3.908	0.368	"	9.6	113

Temp. = 54.8° W = 44.31
K(urea) = 4.05 M_0 = 110

w	Δ*t*	Cor.	%	M
0.949	0.112	0%	2.1	77.4
1.822	0.156	"	4.1	84.6
2.724	0.206	"	6.1	121
3.690	0.266	"	8.3	127

Temp. = 36° W = 40.14
K(calc.) = 3.73 M_0 = 110

w	Δ*t*	Cor.	%	M
0.932	0.185	0%	2.3	46.6
1.936	0.243	"	4.8	74.6
2.791	0.326	"	6.9	79.8

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[1] $4.05\,(308.5/327.8)^2(568/554) = 3.72.$

Temp. = 35° W = 43.46
K(calc.) = 3.71 M_0 = 110

w	Δt	Cor.	%	M
0.661	0.243	0%	1.5	23.1
1.336	0.328	"	3.1	34.7
2.166	0.411	"	5.0	43.9
2.436	0.466	"	5.6	43.8

Succinimid

Temp. = 100° W = 42.02
K(B) = 5.1 M_0 = 99

w	Δt	Cor.	%	M
[0.894	0.103	0%	2.1	105
1.951	0.231	"	4.6	102
2.877	0.342	"	6.8	102
3.935	0.470	"	9.4	102
5.349	0.621	"	12.7	105

Temp. = 75° W = 42.65
K(urea) = 4.32 M_0 = 99

w	Δt	Cor.	%	M
1.106	0.120	0%	2.6	93.3
2.325	0.240	"	5.5	98.3
3.508	0.340	"	8.2	105

Temp. = 54.4° W = 44.02
K(urea) = 4.04 M_0 = 99

w	Δt	Cor.	%	M
1.077	0.114	0%	2.4	86.7
2.133	0.166	"	4.8	118
3.170	0.241	"	7.2	122
4.336	0.323	"	9.8	124

In the first measurement violent foaming. Flame lowered in suceeding measurements. Hence high values(?)

Temp. = 54.6° W = 45.14
K(urea) = 4.04 M_0 = 99

w	Δt	Cor.	%	M
2.538	0.204	0%	5.6	113

Temp. = 36° W = 40.21
K.(calc.)3.73 M_0 = 99

w	Δt	Cor.	%	M
0.914	0.100	0%	2.3	84.5
2.046	0.140	"	5.1	135
3.324	0.170	"	8.3	180

Temp. = 36° W = 39.11
K(calc.) = 3.73 M° = 99.

w	Δt	Cor.	%	M
0.581	0.086	10%	1.5	64.3
1.974	0.156	29 "	5.0	125
2.642	0.222	14 "	6.8	114
3.343	0.295	10 "	8.5	107

Temp. 35° W = 43.08
K(calc. = 3.71 M_0 = 99

0.563 grams dropped in at outset. To be subtracted from given figures.

w	Δt	Cor.	%	M
1.500	0.059	0%	3.5	136
2.542	0.111	"	6.0	152
4.100	0.199	"	9.5	152

Mannite

Temp. = 100° W = 42.55
K(B) = 5.1 M_0 = 182

1.221	0.079	0%	2.9	189
1.829	0.121	"	4.3	185
2.667	0.179	"	6.3	182
3.554	0.233	"	8.2	186

Temp. = 75° W = 43.62
K(urea) = 4.32 M_0 = 182

w	Δt	Cor.	%	M
1.054	0.061	0%	2.4	171
2.094	0.120	"	4.8	173
3.083	0.173	"	7.1	177
4.287	0.242	"	9.8	176

Temp. = 54° W = 43.62
K(urea) = 4.03 M_0 = 182

w	Δ*t*	Cor.	%	M
1.065	0.066	0%	2.4	149
2.164	0.129	"	5.0	155
3.225	0.170	"	7.4	176
4.333	0.226	"	9.9	177

Temp. = 35.5° W = 40.93
K(calc.) = 372 M_0 = 182

w	Δ*t*	Cor.	%	M
0.843	0.053	0%	2.1	155
1.976	0.143	"	4.8	124
2.839	0.207	"	6.9	123

Temp. = 36° W = 41.31
K(calc.) = 3,73 M_0 = 182

w	Δ*t*	Cor.	%	M
1.065	0.095	0%	2.6	101
2.216	0.017	"	5.4	169
3.228	0.189	"	7.8	154

Urethane

Temp. = 100° W = 43,77
K(B) = 5.1 M_0 = 89

w	Δ*t*	Cor.	%	M
0.489	0.031	0%	1.1	184
1.227	0.081	"	2.8	176
2.091	0.141	"	4.8	173
2.581	0.171	"	5.9	176
3.089	0.203	"	7.0	177

Temp. = 75° W = 43.44
K(urea) = 4.32 M_0 = 89

w	Δ*t*	Cor.	%	M
1.961	0.181	0%	4.5	108
2.993	0.243	"	6.9	123
4.062	6.303	"	9.4	133
4.667	0.333	"	10.8	139

Oily streaks observed on sides of boiling tube showing urethane volatilized.

Temp. 54.5° W = 44.60
K(urea) = 4.04 M_0 = 89

w	Δ*t*	Cor.	%	M
0.771	0.170	0%	1.7	41.1
1.598	0.210	"	3.6	69.0
2.400	0.261	"	5.4	83.4
3.202	0.304	"	7.2	95.4
4.014	0.349	"	9.0	104

Temp. = 35° W = 41.82
K(calc.) = 3.71 M_0 = 89

w	Δ*t*	Cor.	%	M
0.784	0.250	0%	1.9	27.8
1.556	0.307	"	3.7	44.8
2.053	0.333	"	4.9	54.5
2.508	0.355	"	6.0	62.4
3.057	0.398	"	7.3	68.1

Temp. = 36° W = 39.57
K(calc.) = 3.73 M_0 = 89

w	Δ*t*	Cor.	%	M
0.853	0.139	0%	2.2	54.6
1.774	0.204	"	4.5	81.7
2.599	0.256	"	6.6	95.5

Methyl Alcohol

Urethane

Temp. = 66° W = 34.22
K(B) = 8.8 M_0 = 89

w	Δ*t*	Cor.	%	M
0.749	0.209	0%	2.2	92.2
1.155	0.320	"	3.4	92.7
3.273	0.880	"	9.6	95.6
4.109	1.098	"	12.0	96.2
5.103	1.340	"	14.9	97.9
6.142	1.592	"	18.0	99.2

Temp. = 44° W = 33.35
K(urethane) = 7.55 M_0 = 89

w	Δt	Cor.	%	M
0.534	0.130	0%	1.6	93.1
1.047	0.269	"	3.1	88.2
1.580	0.409	"	4.7	87.5
2.124	0.546	"	6.4	88.1
2.704	0.692	"	8.1	88.5
3.265	0.831	"	9.8	89.0

Temp. = 35.4° W = 44.89
K(urethane) = 7.55 M_0 = 89

w	Δt	Cor.	%	M
0.560	0.125	0%	1.7	88.1
1.124	0.258	"	3.3	85.9
1.667	0.385	"	4.9	85.3
2.203	0.508	"	6.5	85.5
2.742	0.621	"	8.1	85.8
3.733	0.826	"	11.0	89.0

Acetanilid

Temp. = 66° W = 32.80
K(B) = 8.8 M_0 = 135

w	Δt	Cor.	%	M
0.672	0.130	0%	2.0	136
1.208	0.242	"	3.7	134
1.938	0.385	"	5.9	135
2.643	0.517	"	8.1	137
3.338	0.648	"	10.2	138
4.037	0.772	"	12.3	140

Temp. = 43.5° W = 34.55
K(urethane) = 7.52 M_0 = 135

w	Δt	Cor.	%	M
0.705	0.122	0%	2.0	126
1.290	0.225	"	3.7	125
1.929	0.325	"	5.6	130
2.621	0.434	"	7.6	132
3.284	0.532	"	9.5	135
3.947	0.627	"	11.4	137

Temp. = 25° W = 33.13
K(urethane) = 5.65 M_0 = 135

w	Δt	Cor.	%	M
0.490	0.084	2%	1.5	117
0.888	0.153	0 "	2.7	116
1.300	0.231	3 "	3.9	112
1.735	0.299	3 "	5.2	116
2.111	0.368	3 "	6.4	115

Acenaphthene

Temp. = 66° W = 34.12
K(B) = 8.8 M_0 = 154

w	Δt	Cor.	%	M
0.776	0.112	0	2.3	179
1.568	0.234	"	4.6	173
2.326	0.344	"	6.8	174
3.332	0.456	"	9.8	188

Temp. = 43.4° W = 34.27
K(urethane) = 7.52 M_0 = 154

w	Δt	Cor.	%	M
0.683	0.095	--	2.0	158

23 mins. for solution. Value for M uncertain. Not corrected.

Temp. = 43.4° W = 34.26
K(urethane) = 7.52 M_0 = 154

w	Δt	Cor.	%	M
0.339	0.067	--	1.0	111
0.799	0.135	--	2.3	130
1.129	0.205	--	3.3	120

14 to 28 minutes for solution. Values for M uncertain. Not corrected.

Temp. = 24.8° W = 34.62
K(urethane) = 6.64 M_0 = 154

w	Δt	Cor.	%	M
0.333	0.071	12%	1.0	90.0
0.681	0.113	58 "	2.0	115

Trace of acenaphthene undissolved.

Naphthalene

Temp. = 66° W = 35.35
K(B) = 8.8 M_o = 128

w	Δt	Cor.	%	M
0.560	0.103	10%	1.6	133
1.058	0.187	"	3.0	141
1.586	0.270	"	4.5	146
2.087	0.349	"	5.4	149
2.604	0.423	"	7.9	153
3.551	0.560	"	10.1	158

Temp. = 43.5° W = 34.39
K(urethane) = 6.66 M_o = 128

w	Δt	Cor.	%	M
0.407	0.070	0%	1.2	128
0.850	0.146	"	2.5	128
1.275	0.213	"	3.7	131
1.655	0.282	"	4.8	129
2.018	0.352	"	5.9	126
2.357	0.423	"	6.8	121

Temp. = 25.2° W = 34.11
K(urethane) = 6.66 M_o = 128

w	Δt	Cor.	%	M
0.475	0.080	5%	1.4	115
1.441	0.233	3"	4.2	120
1.927	0.323	15"	5.7	116

Ethyl Alcohol

Urea

Temp. = 78° W = 33.72
K(B) = 11.7 M_o = 60

w	Δt	Cor.	%	M
0.773	0.404	0%	2.3	62.9
1.198	0.639	1"	3.6	65.1
1.696	0.877	0"	5.0	67.1
2.158	1.086	0"	6.4	68.9
2.682	1.306	0"	8.0	71.3
3.251	1.528	1"	9.6	73.8

Temp. = 52.2° W = 34.03
K(calc.) = 9.60[1] M_o = 60

w	Δt	Cor.	%	M
0.556	0.277	10%	1.6	56.6
1.104	0.525	11"	3.2	59.4
1.731	0.776	10"	5.1	62.8
2.381	1.031	9"	7.0	65.1

Temp. = 25° Not soluble enough.

Temp. = 25°. Too insoluble.

Urethane

Temp. = 78° W = 34.94
K(B) = 11.7 M_o = 89

w	Δt	Cor.	%	M
0.495	0.187	0%	1.4	88.7
0.951	0.341	"	2.7	93.4
1.495	0.532	"	4.3	94.1
2.051	0.722	"	5.5	95.1
2.608	0.909	"	7.9	96.1
3.177	1.094	"	9.1	97.2

Temp. = 52.2° W = 33.24
K(B) = 9.60 M_o = 89

w	Δt	Cor.	%	M
0.565	0.189	9%	1.7	86.4
1.154	0.381	"	3.5	87.6
1.704	0.552	"	5.1	89.3
2.793	0.872	"	8.4	92.5
3.388	1.074	"	10.2	93.5

Temp. = 27.6° W = 33.32
K(calc.) = 7.80[1] M_o = 89

w	Δt	Cor.	%	M
0.568	0.175	0%	1.7	76.0
1.166	0.345	0"	3.5	78.7
1.759	0.515	0"	5.3	79.8
2 302	0.660	2"	6.9	81.6
2.868	0.812	3"	8.6	82.6
3.457	0.960	2"	10.4	84.2

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[1] $11.7(325.2/351)^2(204.6/214.2) = 9.60$.

[1] $11.7(300.6/351)^2(204.6/225.2) = 7.80$.

Resorcinol

Temp. = 78° W = 33.16
K(B) = 11.7 M_0 = 110

w	Δt	Cor.	%	M
0.634	0.218	0%	1.9	103
1.268	0.434	"	3.8	103
1.753	0.612	"	5.3	101
2.441	0.865	"	7.4	99.6
3.058	1.100	"	9.2	98.1
3.723	1.360	"	11.2	96.6

Temp. = 52.3° W = 32.90
K(calc.) = 9 60 M_0 = 110

w	Δt	Cor.	%	M
0.579	0.172	0%	1.7	98.4
1.217	0.378	"	3.7	93.9
1.806	0.566	"	5.5	93.0
2.473	0.784	"	7.5	92.0
3.018	0.969	"	9.2	90.8
3.640	1.181	"	11.1	89.8

Temp. = 27.8° W = 33.19
K(calc.) = 7.81 M_0 = 110

w	Δt	Cor.	%	M
0.671	0.199	3%	2.0	79.3
1.475	0.422	2 "	4.4	82.2
2.344	0.672	0 "	7.1	82.0
3.162	0.911	2 "	9.5	81.6
3.826	1.145	0 "	11.5	78.5
4.484	1.327	0 "	13.5	83.3

Benzamid

Temp. = 78° W = 33.36
K(B) = 11.7 M_0 = 121

w	Δt	Cor.	%	M
0.929	0.269	0%	2.8	121
1.959	0.559	"	5.9	123
2.794	0.778	"	8.4	126
3.631	0.990	"	10.9	129
4.476	1.192	"	13.4	132
5.335	1.395	"	16.0	134

Temp. = 52.2° W = 32.82
K(calc.) = 9.60 M_0 = 121

w	Δt	Cor.	%	M
0.655	0.164	0%	2.0	116
1.276	0.305	"	3.9	122
1.991	0.464	"	6.1	125
2.557	0.584	"	7.8	128
3.018	0.694	"	9.2	127
3.607	0.824	"	11.0	128

Temp. 27.8° W = 34.29
K(calc.) = 7.81 M_0 = 121

w	Δt	Cor.	%	M
0.648	0.168	5 "	1.9	87.8
1.226	0.319	3 "	3.6	87.5
1.794	0.456	3 "	5.2	89.8

In the last measurement the solution was saturated and some benzamid crystallized on walls of boiling tube above the solution so result is a little too high.

p-Toluidin

Temp. = 78° W = 31.97
K(B) = 11.7 M_0 = 107

w	Δt	Cor.	%	M
0.534	0.189	0%	1.7	103
1.079	0.365	"	3.4	108
1.589	0.530	"	5.0	110
2.139	0.695	"	6.7	113
2.683	0.859	"	8.4	114
3.225	1.011	"	10.1	117

Tem. = 52.2° W = 32.85
K(calc.) = 9.60 M_0 = 107

w	Δt	Cor.	%	M
0.555	0.167	0%	1.7	97.4
1.103	0.311	"	3.4	103
1.609	0.438	"	4.9	107
2.160	0.577	"	6.6	109
2.676	0.705	"	8.1	111
3.195	0.827	"	9.7	113

Temp. = 27.5° W = 34.79
K. (calc.) = 7.79 M_0 = 107

w	Δt	Cor.	%	M
0.548	0.146	0%	1.5	84.0
1.244	0.308	3 "	3.6	90.4
2.027	0.478	1 "	5.8	94.5
2.773	0.634	0 "	7.9	98.1
3.539	0.788	0 "	10.1	101
4.301	0.930	0 "	12.3	104

Acetanilid

Temp. = 78° W = 32.99
K(B) = 11.7 M_0 = 135

w	Δt	Cor.	%	M
0.977	0.259	0%	3.0	134
1.449	0.382	"	4.4	134
2.150	0.557	"	6.5	137
2.882	0.733	"	8.7	139
3.689	0.921	"	11.2	142
4.836	1.178	"	14.7	145

Temp. = 52° W = 34.05
K(calc.) = 9.59 M_0 = 135

w	Δt	Cor.	%	M
0.579	0.120	0%	1.7	137
1.225	0.257	0 "	3.6	136
1.922	0.391	0 "	5.7	140
2.573	0.523	1 "	7.6	140

Temp. = 27.7° W = 32.94
K(calc.) = 7.81 M_0 = 135

w	Δt	Cor.	%	M
0.626	0.129	8%	1.9	114
1.300	0.253	11 "	4.0	121
1.925	0.370	2 "	5.9	123
2.563	0.485	4 "	7.8	125
3.199	0.591	8 "	9.7	128

Acenaphthene

Temp. = 78° W = 31.14
K(B) = 11.7 M_0 = 154

w	Δt	Cor.	%	M
1.089	0.250	0%	3.5	164
1.886	0.419	0 "	6.0	169
2.637	0.559	0 "	8.4	177
3.363	0.684	0 "	10.8	185
4.120	0.809	0 "	13.2	191
4.875	0.916	1 "	15.7	200

Temp. = 52° W = 34.57
K(calc.) = 9.59 M_0 = 154

w	Δt	Cor.	%	M
0.480	0.099	0%	1.4	135
1.002	0.200	0 "	2.9	140
1.527	0.291	33 "	4.4	145
2.073	0.408	28 "	6.0	142
2.590	0.451	16 "	7.5	159
3.160	0.587	14 "	9.1	149

Temp. 28°. Too insoluble.

Naphthalene

Temp. = 78° W = 32.49
K(B) = 11.7 M_0 = 128

w	Δt	Cor.	%	M
0.826	0.215	0%	2.5	138
1.606	0.404	"	4.9	143
2.397	0.575	"	7.4	150
3.182	0.740	"	9.8	155
4.036	0.909	"	12.4	160
4.831	1.061	"	14.9	164

Temp. = 52.2° W = 33.17
K(calc.) = 9.60 M_0 = 128

w	Δt	Cor.	%	M
0.552	0.128	0%	1.7	125
1.344	0.298	0 "	4.0	131
2.147	0.458	0 "	6.5	136
2.923	0.601	0 "	8.8	140
3.663	0.738	1 "	11.0	143
4.465	0.892	2 "	13.5	145

Temp. = 27.5° W = 33.54
K(calc.) = 7.79 M_0 = 128

w	Δ*t*	Cor.	%	M
0.676	0.151	4%	2.0	104
1.419	0.293	10 "	4.2	113
2.114	0.414	16 "	6.3	118
2.844	0.533	5 "	8.5	124

Naphthalene volatized and crystallized on upper part of boiling tube so results are somewhat uncertain, in last measurement at any rate.

Phenanthrene

Temp. = 78° W = 34.05
K(B) = 11.7 M_0 = 178

w	Δ*t*	Cor.	%	M
0.519	0.100	0 "	1.5	178
1.482	0.270	0 "	4.4	189
2.122	0.374	2 "	6.2	195
3.050	0.506	1 "	9.0	207
3.747	0.594	0 "	11.0	217
4.802	0.716	0 "	14.1	230

Temp. = 51.8° W = 33.17
K(B) = 9.58 M_0 = 178

w	Δ*t*	Cor.	%	M
0.488	0.099	0%	1.5	142
1.009	0.190	0 "	3.0	154
1.591	0.280	0 "	4.8	164
2.111	0.361	0 "	6.4	169
2.608	0.414	23 "	7.9	182

Temp. 28°. Too insoluble.

Succinimid

Temp. 78° W = 33.46
K(B) = 11.7 M_0 = 99

w	Δ*t*	Cor.	%	M
0.933	0.317	0%	2.8	103
1.748	0.569	"	5.2	107
2.391	0.751	"	7.1	111
3.094	0.938	"	9.2	115
4.068	1.180	"	12.1	121
5.058	1.408	"	15.1	156

Temp. 52.3° W = 35.03
K(calc.) = 9.61 M_0 = 99

w	Δ*t*	Cor.	%	M
0.717	0.196	4%	2.0	100
1.419	0.381	3 "	4.0	102
2.145	0.556	7 "	6.1	106
2.833	0.719	3 "	8.1	108

Temp. 28°. Too insoluble.

Propyl Alcohol

Urethane

Temp. = 97° W = 34.17
K(B) = 16.09 M_0 = 89

w	Δ*t*	Cor.	%	M
0.564	0.277	0%	1.7	95.8
1.151	0.557	"	3.4	97.2
1.740	0.824	"	5.1	99.3
2.297	1.076	"	6.7	100
2.878	1.328	"	8.4	102
3.462	1.574	"	10.1	103

Temp. = 64.7° W = 34.38
K(calc.) = 13.40[1] M_0 = 89

w	Δ*t*	Cor.	%	M
0.651	0.264	0%	1.9	95.9
1.290	0.523	"	3.8	95.9
1.946	0.780	"	5.7	97.0
2.567	1.008	"	7.5	99.0
3.186	1.224	"	9.3	103
3.837	1.452	"	11.2	103

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[1] $16.09(337.7/370)^2 = 13.40$; no data found for change of *q* with T.

Temp. 36.5° W = 35.70
K(calc.) = 11.26[1] M_0 = 89

w	Δ*t*	Cor.	%	M
0.592	0.206	0%	1.7	90.4
1.123	0.386	0 "	3.3	91.5
1.683	0.582	0 "	4.9	91.0
2.281	0.757	1 "	6.6	94.8
2.826	0.910	3 "	8.2	97.6
3.462	1.084	1 "	10.1	100

---

[1] $16.09(309.5/370)^2 = 11.26$.

Naphthalene

Temp. = 97° W = 33.02
K(B) = 16.09 M_0 = 128

w	Δt	Cor.	%	M
0.816	0.270	0%	2.5	147
1.639	0.525	"	5.0	152
2.411	0.744	"	7.3	158
3.330	0.989	"	10.1	164
4.143	1.203	"	12.6	168
4.894	1.385	"	14.8	172

Temp. = 64.1° W = 34.18
K(calc.) = 13.36 M_0 = 128

w	Δt	Cor.	%	M
0.580	0.160	2%	1.7	142
1.145	0.303	3 "	3.3	148
1.691	0.431	2 "	4.9	153
2.271	0.561	2 "	6.6	158
2.881	0.690	4 "	8.4	163
3.509	0.815	1 "	10.3	168

Temp. = 36.9° W = 33.90
K(calc.) = 11.29 M_0 = 128

w	Δt	Cor.	%	M
0.703	0.157	4 "	2.1	149
1.425	0.292	16 "	4.2	162
2.164	0.439	12 "	6.4	164
2.796	0.526	20 "	8.3	176

Acenaphthene

Temp. = 97° W = 32.00
C(B) = 16.09 M_0 = 154

w	Δt	Cor.	%	M
0.556	0.173	0%	1.7	162
1.114	0.326	"	3.5	172
1.635	0.469	"	5.1	175
2.160	0.607	"	6.8	179
2.871	0.787	"	9.0	183
3.226	0.875	"	10.1	185

Temp. = 63.9° W = 33.46
K(calc.) 13.35 M_0 = 154

w	Δt	Cor.	%	M
0.568	0.135	1%	1.7	167
1.181	0.274	3 "	3.5	171
1.673	0.371	3 "	5.0	179
2.218	0.476	6 "	6.6	185
2.790	0.585	6 "	8.3	189
3.333	0.688	1 "	9.9	192

Acenaphthene crystallized on cooling from last solution. Temp. = 36°. Too insoluble.

Chloroform

Urethane

Temp. = 61.7° W = 60.34
K(naphthalene) = 37.86 M_0 = 89

w	Δt	Cor.	%	M
0.610	0.390	0%	1.0	98.0
1.205	0.731	"	2.0	103
1.736	1.003	"	2.9	108
2.322	1.287	"	3.8	110
2.940	1.570	"	4.9	116
3.544	1.821	"	5.9	122

Temp. = 42.7° W = 59.40
K(naphthalene) = 34.33 M_0 = 89

w	Δt	Cor.	%	M
0.645	0.360	0%	1.0	104
1.271	0.654	"	2.1	112
1.908	0.925	"	3.2	119
2.524	1.163	"	4.3	125
3.143	1.396	"	5.3	131
3.734	1.610	"	6.3	134

Temp. = 26.6° W = 60.48
K(naphthalene) = 30.09 M_0 = 89

w	Δt	Cor.	%	M
0.511	0.255	0%	0.8	99.7
1.035	0.479	"	1.7	108
1.584	0.689	"	2.6	115
2.107	0.873	"	3.5	120
2.618	1.046	"	4.3	125
3.103	1.202	"	5.1	128

Acetanilid

Temp. = 61.7° W = 59.27
K(naphthalene) = 37.86 M_o = 135

w	Δt	Cor.	%	M
0.832	0.346	0%	1.4	154
1.448	0.556	"	2.4	167
2.168	0.763	"	3.7	181
2.888	0.940	"	4.9	196
3.563	1.094	"	6.0	208
4.233	1.233	"	7.1	219

Temp. = 42.3° W = 58.41
K(naphthalene) = 34 24 M_o = 135

w	Δt	Cor.	%	M
0.468	0.189	0%	0.8	146
0.986	0.357	"	1.7	162
1.524	0.503	"	2.6	178
2.122	0.640	"	3.6	195
2.718	0.760	"	4.6	220
3.452	0.898	"	5.9	226

Temp. = 26.3° W = 57.78
K(naphthalene) = 30.05 M_o = 135

w	Δt	Cor.	%	M
0.676	0.232	0%	1.2	151
1.320	0.397	"	1.3	165
2.039	0.547	"	3.5	193
2.739	0.659	"	4.7	216
3.466	0.765	"	6.0	236
3.966	0.862	"	6.9	240

Acenaphthene

Temp. = 61.7° W = 60.84
K(naphthalene) = 37.86 M_o = 154

w	Δt	Cor.	%	M
0.413	0.172	0%	0.7	150
0.769	0.323	"	1.3	148
1.115	0.470	"	1.8	148
1.460	0.610	"	2.4	149
1.780	0.743	"	2.9	149
2.412	1.000	"	4.0	150

Naphthalene

Temp. = 61.7° W = 60.53
K(naphthalene) = 37.86 M_o = 128

w	Δt	Cor.	%	M
0.644	0.318	0%	1.1	127
1.256	0.621	"	2.1	127
1.845	0.914	"	3.0	127
2.468	1.210	"	4.1	128
3.037	1.488	"	5.0	128
3.620	1.769	"	6.0	128

Temp. = 42.9° W = 58.20
K(naphthalene) = 34.36 M_o = 128

w	Δt	Cor.	%	M
0.558	0.267	0%	1.0	123
1.084	0.509	0 "	1.9	125
1.643	0.769	0 "	2.8	126
2.093	0.972	1 "	3.6	127
2.702	1.246	1 "	4.6	128
3.302	1.523	1 "	5.7	128

Temp. = 26.7° W = 55.88
K(naphthalene) = 30.11 M_o = 128

w	Δt	Cor.	%	M
0.617	0.249	3%	1.1	133
1.197	0.503	0 "	2.1	128
1.712	0.734	0 "	3.1	126
2.269	0.965	0 "	4.1	127
2.829	1.185	0 "	5.1	129
3.419	1.439	1 "	6.1	128

p-Toluidin

Temp. = 61.7° W = 54.71
K(naphthalene) = 37.86 M_o = 107

w	Δt	Cor.	%	M
0.523	0.347	0%	1.0	104
1.093	0.725	"	2.0	104
1.630	1.046	"	3.0	107
2.155	1.405	"	3.9	106
2.635	1.705	"	4.8	106
3.155	2.033	"	5.8	107

In all the measurements with *p*-toluidin, chloroform had been standing for some time and give a slight precipitate for chlorin with silver nitrate.

Temp. = 42.7° W = 59.44
K(naphthalene) = 34.33 $M_o = 107$

w	Δt	Cor.	%	M
0.534	0.261	0%	0.9	118
1.034	0.533	"	1.8	112
1.564	0.815	"	2.6	111
2.094	1.082	"	3.7	111
2.648	1.356	"	4.5	112
3.164	1.630	"	5.3	112

Temp. = 26.3° W = 61.33
K(naphthalene) = 30,04 $M_o = 107$

w	Δt	Cor.	%	M
0.475	0.203	0%	0.8	115
0.984	0.444	"	1.6	108
1.493	0.673	"	2.4	108
1.997	0.900	"	3.3	108
2.527	1.127	"	4.1	109
3.083	1.376	"	5.0	109

Toluene

Urethane

Temp. = 110.8° W = 37.84
K.(calc.) = 33.94[1] $M_o = 89$

w	Δt	Cor.	%	M
0.546	0.197	none	1.5	247
1.030	0.378	"	2.7	244
1.582	0.577	"	4.2	245
2.111	0.768	"	5.6	246
2.556	0.927	"	6.7	242
3.901	1.363	"	10.3	254

Temp. = 80.1° W = 36.44
K(calc.) = 28.71 $M_o = 89$

$K = 33.94\,(353/383.8)^2 = 28.71$

w	Δt	Cor.	%	M
0.522	0.213	0%	1.4	194
1.042	0.416	"	2.9	197
1.818	0.689	"	5.0	207
2.672	0.950	"	7.3	221
3.553	1.190	"	9.8	235
4.016	1.310	"	11.0	242

Temp. 25.0° W = 35.32
K(calc.) = 25.04[1] $M_o = 89$

w	Δt	Cor.	%	M
0.641	0.242	0%	1.8	187
1.089	0.296	"	3.1	194
1.541	0.539	"	4.4	203
1.963	0.664	"	5.6	210
2.410	0.780	"	6.8	219
2.898	0.903	"	8.2	227

[1] $33.94(329.7/383.8)^2 = 25.04.$

Temp. = 34.2° W = 36.79
K(calc.) = 21.74[1] $M_o = 89$

w	Δt	Cor.	%	M
0.550	0.212	0%	1.5	153
1.727	0.529	"	4.7	193
2.942	0.793	"	8.0	219
3.502	0.916	"	9.5	226

[1] $33.94(307.2/383.8)^2 = 21.74$

p-Toluidin

Temp. = 110.8° W = 37.13
K(calc.) = 33.94 $M_o = 107$

w	Δt	Cor.	%	M
0.417	0.301	0%	1.1	127
0.947	0.692	"	2.6	126
1.507	1.099	"	4.1	126
2.050	1.487	"	5.5	127
2.549	1.835	"	6.9	127
2.975	2.115	"	8.0	129

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[1] Beckmann does not list toluene. According to Ramsay and Marshall, $q = 86.8$, at 110.8° so

$$K = 0.02(383.8)^2/86.8 = 33.94$$

Temp. = 80.5° W = 35.74
K(calc.) = 28.81 M_0 = 107

w	Δt	Cor.	%	M
0.489	0.329	0%	1.4	120
0.996	0.668	"	2.8	120
1.473	0.970	"	4.1	122
1.996	1.297	"	5.6	123
2.447	1.580	"	6.9	125
3.075	1.942	"	8.6	127

Temp. = 56.7° W = 36.95
K(calc.) = 25.04 M_0 = 107

w	Δt	Cor.	%	M
0.497	0.298	0%	1.3	113
0.964	0.568	"	2.6	113
1.514	0.872	"	4.1	115
2.026	1.146	"	5.5	121
2.537	1.405	"	6.9	123
3.065	1.669	"	8.3	125

Temp. = 34.6° W = 38.08
K(calc.) = 21.84 M_0 = 107

w	Δt	Cor.	%	M
0.530	0.304	0%	1.4	100
0.987	0.550	"	2.6	103
1.532	0.844	"	4.0	104
2.053	1.094	"	5.4	108
2.610	1.347	"	6.8	111
3.167	1.601	"	8.3	113

Acenaphthene

Temp. = 110.8° W = 36.62
K(calc.) = 33.94 M_0 = 154

w	Δt	Cor.	%	M
0.547	0.332	0%	1.5	153
1.034	0.622	"	2.8	155
1.415	0.851	"	3.9	154
1.753	1.051	"	4.8	155
2.452	1.452	"	6.7	157
3.094	1.811	"	8.5	159

Temp. = 80.5° W = 36.48
K(calc.) = 28.81 M_0 = 154

w	Δt	Cor.	%	M
0.637	0.326	0%	1.8	154
1.329	0.680	"	3.6	154
1.963	0.978	"	5.4	155
3.331	1.620	"	9.1	163
4.174	2.005	"	11.4	165

Solution foamed.

Temp. = 56.4° W = 35.35
K(calc.) = 25.07 M_0 = 154

w	Δt	Cor.	%	M
0.614	0.299	0%	1.7	147
1.232	0.579	"	3.5	154
1.862	0.842	"	5.3	157
2.422	1.080	"	6.9	159
3.065	1.352	"	8.7	161
3.716	1.621	"	10.5	162

Solution foamed.

Temp. = 34.6° W = 37.36
K(calc.) = 21.84 M_0 = 154

w	Δt	Cor.	%	M
0.570	0.206	0%	1.5	161
1.158	0.451	"	3.1	150
1.800	0.673	"	4.8	157
2.370	0.878	"	6.3	158
2.980	1.096	"	8.0	159
3.618	1.302	"	9.7	162

Solution foamed badly; last two values uncertain.

Phenanthrene

Temp. = 110.8° W = 38.30
K(calc.) = 33.94 M_0 = 178

w	Δt	Cor.	%	M
0.550	0.272	0%	1.4	178
1.120	0.550	"	2.9	179
1.634	0.787	"	4.3	183
2.788	1.295	"	7.3	195

Temp. = 80.5° W = 36.23
K(calc.) = 28.81 M_0 = 178

w	Δt	Cor.	%	M
0.638	0.311	0%	1.8	163
1.303	0.621	"	3.6	167
1.941	0.914	"	5.4	169
2.609	1.218	"	7.2	170
3.277	1.501	"	9.0	174
3.936	1.779	"	10.9	176

Solution foamed.

Temp. = 57.0° W = 36.01
K(calc.) = 25.14 M_0 = 178

w	Δt	Cor.	%	M
0.520	0.219	0%	1.4	165
1.833	0.782	"	5.1	164
2.532	1.039	"	7.0	170
3.323	1.328	"	9.2	174
4.095	1.593	"	11.4	179

Solution foamed.

Temp. = 34.3° W = 38.70
K(calc.) = 21.74 M_0 = 178

w	Δt	Cor.	%	M
0.791	0.373(?)	0%	2.0	120(?)
1.418	0.198	"	3.7	179
2.091	0.398	"	5.4	184
2.794	0.598	"	7.2	192
3.459	0.792	"	8.9	191
4.072	0.962	"	10.5	193

Foamed very badly, so results are not certain. First result so different from others that it is calculated separately.

Naphthalene

Temp. = 110.8° W = 36.55
K(calc.) = 33.94 M_0 = 128

w	Δt	Cor.	%	M
0.706	0.479	0%	1.9	136
1.197	0.820	"	3.3	135
1.679	1.139	"	4.6	136
2.161	1.452	"	5.9	137
2.615	1.751	"	7.2	137
3.447	2.264	"	9.4	141

Temp. = 81.0° W = 36.15
K(calc.) = 28.91 M_0 = 128

w	Δt	Cor.	%	M
0.743	0.442	0%	2.1	134
1.442	0.854	"	4.0	135
2.242	1.313	"	6.2	136
3.030	1.750	"	8.4	138
3.843	2.190	"	10.6	139
4.604	2.597	"	12.8	142

Temp. = 56.7° W = 38.62
K(calc.) = 25.04 M_0 = 128

w	Δt	Cor.	%	M
0.502	0.260	0%	1.3	125
1.022	0.526	"	2.6	124
1.616	0.792	"	4.2	134
2.211	1.062	"	5.7	136
2.792	1.322	"	7.2	137
3.411	1.599	"	8.8	139

Temp. = 35.0° W = 36.76
K(calc.) = 21.94 M_0 = 128

w	Δt	Cor.	%	M
0.527	0.238	0%	1.4	132
1.064	0.494	"	2.9	129
1.590	0.722	"	4.3	132
2.156	0.949	"	5.9	135
2.740	1.192	"	7.4	137
3.323	1.460	"	9.0	135

Foamed. Last value uncertain.

Rutgers College, September, 1897

SOLUBILITY AND BOILING-POINT

BY OLIVER W. BROWN

It has been shown by Steuber[1] that, when sodium chlorid or sugar is added to aqueous alcohol, the salt and the sugar increase the partial pressure of the alcohol and the boiling point does not rise as much as when pure water is taken. A natural conclusion to be drawn from these experiments is that the disturbing influence of the alcohol would be less if the substance added were soluble both in alcohol and in water. This can readily be realized with urea and, at the suggestion of Professor Bancroft, I have made some boiling point determinations with potasssium chlorid and with urea in aqueous alcohol. Urea is especially adapted for such work because it gives excellent results with pure water. The measurements were made with the Beckmann apparatus.

The results with potassium chlorid are given in Table I. In the table g denotes the grams of salt in one hundred grams of aqueous alcohol and Δ the rise of boiling point. The concentration of the aqueous alcohol was not determined accurately but was roughly fifty percent by volume.

TABLE I

Barometer 741.6 mm

g	Δ	$-g/\Delta$
0.6054	−0.06°	10.09
1.1910	−0.13	9.16
1.8406	−0.18	10.22
2.4984	−0.25	9.99

It is seen from this table that the addition of potassium chlorid low-

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[1] Jour. Phys. Chem. 1, 643, 1897.

ers the boiling point instead of raising it[1] and that the lowering is proportional to the concentration for this particular case.

The aqueous alcohol used in the determinations with urea was also about fifty percent by volume, that used for the experiments recorded in Table II being, however a little more dilute than that used for the experiments in Table III. In both these tables g denotes the number of grams of urea in hundred grams of aqueous alcohol; Δ the rise of boiling point and K a constant calculated from the formula, $K = M\frac{\Delta}{g}$, where M is the reacting weight of urea.

TABLE II

Barometer 744.5 mm

g	Δ	K
0.7022	0.06°	5.126
1.4712	0.10	4.078
2.3509	0.13	3.317
3.2923	0.20	3.644

TABLE III

Barometer 744.8 mm

g	Δ	K
0.3706	0.026°	4.209
1.1200	0.070	3.750
2.3058	0.141	3.660
3.6562	0.210	3.446
6.2713	0.370	3.539

It will be noticed that the boiling point rises, in sharp contradistinction to the experiments with potassium chlorid. The values for K decrease with increasing concentration and seem to pass through a minimum just before the last measurement in each table. This calls for further investigation. It is a rather interesting fact that for these particular mixtures of alcohol and water the values of K for infinite dilution are almost identical with the value 5.2 which

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[1] This has already been observed. Miller. Jour. Phys. Chem. 1, 641 (1897).

would be obtained if we had pure water instead of aqueous alcohol. It seems probable that this is only a coincidence but a more extended study of this point is now being made in this laboratory. With dilute solutions of aqueous alcohol the difference between the behavior of potassium chlorid and of urea would not be so marked. The potassium chlorid would reduce the partial pressure of the water vapor and increase that of the alcohol vapor. The urea would lower the partial pressure of the water to a less extent than did the potassium chlorid, but, on the other hand, it would also decrease the partial pressure of the alcohol. What the result would be in the two cases can not be predicted as yet. With fifty percent alcohol it has been shown that the two substances produce very different effects. It is conceivable however that concentrations might be found such that addition of equivalent quantities of potassium chlorid and of urea might produce equal changes in the boiling point. The partial pressures would not be the same in the two cases, though the total pressures would be.

Cornell University

CORRECTION

BY WILDER D. BANCROFT

My attention has been called by Professor H. W. Bakhuis Roozeboom to the fact that lead iodid crystallizes in the anhydrous form from aqueous solutions, and not with two of water. In my book (The Phase Rule) and Mr. Talmadge's paper[1] lead iodid should be substituted in all cases where hydrated lead iodid occurs. In my second paper on Solids and Vapors[2] the special conclusions based on the assumption of hydrated lead iodid as a solid phase become valueless except in so far as they illustrate the method of attacking such problems.

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[1] Jour. Phys. Chem. **1**, 493 (1897).

[2] Jour. Phys. Chem. **1**, 344 (1897).

NEW BOOKS

Philosophy of Knowledge: *an Inquiry into the Nature, Limits and Validity of Human Cognitive Faculty. By George Trumbull Ladd, Professor of Philosophy in Yale University. New York; Charles Scribner's Sons. 1897. pp. xv., 614. Price $4.00.* Professor Ladd's philosophical works fall into two groups. On the one side we have the *Elements of Physiological Psychology*, the *Psychology, Descriptive and Explanatory*, and the *Philosophy of Mind*. On the other stand the *Introduction to Philosophy* and the present volume; the *Philosophy of Mind* serving in some sense as a bridge between the special philosophy of the psychologist and general philosophy. An ‹Ontology› is yet lacking to the completion of the total system.

Professor Ladd thus comes upon the epistemological field with all the authority of a veteran campaigner in the territory of philosophy. It may be said at once that his work has received high praise from philosophical reviewers,—praise which, so far as I am competent to judge, appears to be wholly merited. Nevertheless, I cannot but doubt whether the doctrines of the book will prove as palatable to the scientific man as to the philosopher *von Fach*.

Nothing is more characteristic of current German epistemology than its intimate relation to the special sciences. Men of the first rank in science—Helmholtz, Ostwald, Mach—have made definite and valuable contributions to the theory of knowledge; while the three schools of empiriocriticism and of immanent and critical realism have the facts and principles of science constantly in mind. Professor Ladd's view, on the contrary, is a purely philosophical view, in which the two influences most distinctly traceable are those of Descartes and of Lotze. Moreover, he is confessedly out of sympathy with modern science. Psychophysical parallelism he cannot away with; yet it is but a harmless working hypothesis, adopted by the experimental psychologist for the services that it renders on the scientific plane. And consider the following passage:

> ‹‹I have several times already expressed my conviction that [the physical and natural] sciences are more than ever full to the brim, and ready to burst, with ontological conceptions and assumptions of most portentous dimensions and uncertain validity. Surely scepticism and agnosticism, now nearly sated with feeding upon the ancient body of alleged truths in ethics and religion,

> will soon turn their devouring maw upon the structure generated and nourished by the modern scientific spirit as dominant in chemico-physical and biological researches. And if the strength of their appetite and the vigor of their digestion remain unimpaired, must we not fear that even the bones of this structure will disappear from our view?» (P. 372, *n.*)

Not by external attacks made in this mood of scorn, but by reverent and sympathetic reconstruction from within, will the reconciliation of science and philosophy be effected. And every intemperate attack that has the weight of philosophical authority behind it serves to delay our final understanding of the universe.

As things are, however, a man may do good service in philosophy despite his quarrel with the methods and pretensions of science. The critics are agreed, as it would be strange if they were not, that Professor Ladd's volume, though not the pioneer work that it professes to be, is at least a solid and noteworthy addition to the literature of epistemology. I cannot better end this brief notice than by quoting a few pregnant sentences in which the author's teaching is summed up:

> «While the knowledge of Self may attain an intuitive penetration to the heart of Reality, the knowledge of Things remains an analogical interpretation of their apparent behavior into terms of a real nature corresponding, in important characteristics, to our own» (227). «What is it *really* to be related? What relates; and what is related? . . . No answers can be given to such questions, unless things are conceived of as self-active beings, with their various modes of behavior interdependent and yet united under a framework . . . of immanent ideas. . . . Therefore, a true and full knowledge of Self is the prime condition of a valid . . . knowledge of all Being» (360–1). «Human cognition is all to be understood as a species of intercourse between minds. In all man's knowledge the real being of the finite Self is in actual commerce with the Absolute Self. This relation of an intercourse between Selves is the one fundamental and permanent conception under which may be truthfully included all the particular forms of relation of which we have experience in the development of the life of cognitions». (558)

E. B. Titchener

Lehrbuch der allgemeinen Chemie. *W. Ostwald. Second edition. Vol. II, Part 2. Second instalment. Large octavo, 208 pages. W. Engelmann; Leipzig, 1897. Price 5 marks.* The continuation of the discussion of reaction velocities takes up nearly one half of the present number. Under this head are to be found bimolecular and trimolecular reactions; methods of determining the order of reaction including a new one by the author for which no data are available; abnormal reactions and the effects of secondary disturbances. The paragraphs on catalytic accelerators and retarders are interesting reading though one fails to find any reference to the catalytic effect of the solvent. The treatment of reversible reactions comes next and is followed by a study of reaction velocities in heterogeneous systems. The pages are filled with equations and with cuts; there is much which is new and more which is interesting so that no one can read this part of the volume without profit to himself. For all that, the matter is disappointing. We have waited long and patiently for this last volume; we have hoped and have had reason to expect that it would be a masterpiece. We have read the enormous mass of material which has been published during the last ten years and we have appreciated the difficulties to be overcome in presenting this matter in an orderly fashion, separating the chaff from the wheat. It has seemed a task which no one save Ostwald could hope to accomplish; but which he could carry through successfully. It is with feelings of sorrow that we perceive that the whole plan of the book has been changed without warning. There is no attempt made even to give references to all the literature on reaction velocities. A few typical cases are cited, the general equations are given for a number of cases which have not yet been studied and—that is all. It seems to the reviewer that it is very desirable to emphasize the fact that the general laws describing reaction velocities apply to all chemical reactions. In the past few years a number of radically different reactions have been studied and found to take place as predicted by the theory. As typical instances we may take the decomposition of the diazo compounds, the change of the synaldoxime acetates and the action of alcoholic carbon bisulfid on bases and alcoholates. None of these are referred to and the list of omissions might be extended very considerably. It may be that these are to be considered in some later number and that we may find at the same time some reference to the action of the solvent. It is certain however that these things are not where they should be, in this number.

After finishing with reaction velocities, the author turns to chemical equilibrium. The phase rule is taken, very properly, as the basis of classification ; but divariant one-component systems are taken up before nonvariant or monovariant systems. Some new definitions are introduced, the substances on the two sides of a reaction equation being termed «hylotropic groups». These groups are then classified according to the number of constituents as being of the first, second or of some higher order. The advantages of this are not made evident. The discussion of the existence of different modifications in the liquid and gaseous phases is of the greatest value and deserves most careful study. The author has overlooked the fact however that if two liquid modifications are possible it no longer follows that the highest melting point represents a state of stable equilibrium. The question of the possibility of a critical point for the equilibrium between solid and liquid is considered at length and it is a pleasure to note the way in which many isolated facts, notably the fluid crystals of Lehmann, are made to support the hypothesis. It is unfortunate that the recent speculations of Tammann were published too late to be mentioned in the text.

The paragraphs on semipermeable walls are interesting and characteristic. A semipermeable wall is defined as a device for enabling one to maintain two pressures in different parts of the system, the question of permeability disappearing entirely. The author then proves by means of «energetics» that if a compressed gas be allowed to act upon a liquid in which it is only sparingly soluble the vapor pressure of the liquid will be increased by an amount which depends on the pressure of the gas and is independent of the nature. In support of this theorem the author cites the recent experiments of Villard and others. These experiments show however that the increase of the vapor pressure of the liquid varies markedly with the nature of the gas. It would have been simpler to have recognized the solvent action of gases and to have omitted the deduction.

An elaborate discussion of the phenomena of supercooled liquids is next in order and the number comes to an end before very much has been said about the existence of two or more solid modifications. The chapter on chemical equilibrium can be summed up very briefly. It is full of brilliant comments but there is no distinction made between exact and inexact theory. *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 which bear upon any phase of Physical Chemistry.

Structure Phenomena

Experiments with Röntgen Rays. *A. Voller and B. Walter. Wied. Ann.* **61**, *88* (*1897*). A Crookes' tube with very high vacuum is a good source of the rays, and gives off but little heat; tubes have been constructed which could be used continuously for an hour without becoming sensibly warm.

Reproductions are given of two photographic plates of the shadows cast by twenty-two substances, the first set being taken with a cool tube and the other with the same tube warmed (from without). The rays from the cool tube, although producing no more effect on the unprotected plate than those from the other, evinced much greater power of penetrating the specimens.

Many attempts have been made to measure the wave length of the Röntgen rays by means of certain phenomena generally ascribed to optical interference. The results so obtained by various investigators differ very widely, and the authors adduce evidence to show that the phenomena in question are not due to interference at all. On the other hand, as the refractive index of the diamond (for ordinary light 2.4 to 2.5) is found to be $1 + 0.0002$, an application of Helmholtz's theory of dispersion shows that, if Röntgen's rays consist of transverse waves, their length can not exceed one one-millionth of a millimeter.

The ability to cause diffuse reflection of the rays was tested with twenty-one chemical elements, and appears to stand in close connection with the position of the latter in Mendelejeff's table. *W. L. M.*

Cathode and Röntgen Rays. *J. Precht. Wied. Ann.* **61**, *330* (*1897*). The paper begins with a series of photographic records of the paths of the cathode rays under the influence of magnets: the results agree with the requirements of Biot-Savart's law.

Turning to Röntgen's rays, the author confirms the conclusions of other experimenters with respect to their non-refrangibility and their action on a steam jet and on a selenium cell: he finds that the degree of fluorescence caused by them depends largely on the presence of slight impurities in the fluorescent substances, and that in certain cases it requires some time to reach its maximum. Calcium platinocyanid is the most fluorescent substance met with but the potassium salt is best for increasing the sensibility of photographic plates.

Photographs of a large number of minerals show that their transparency to the Röntgen rays depends not merely on their thickness and density, but also on their chemical composition.

The Röntgen rays differ from the cathode rays in producing no coloration in crystals of sodium chlorid, and from Lenard's rays in exciting no fluorescence in pentadecyl-paratolyl-ketone.

Lastly, a study of certain interference phenomena (?) leads to a wave length of $370 - 850 \times 10.^{-6}$ «As transverse waves of these lengths can not penetrate paper, Röntgen's rays probably consist, in part at least, of longitudinal waves». *W. L. M.*

On the Absorption of Light by Crystals. *V. Agafonow. Comtes rendus*, **125**, *87* (*1897*). With pure compounds the absorption at the violet end increases with the complexity of the salt. No data are given. *W. D. B.*

On the Change of Salts by Cathode Rays. *R. Abegg. Zeit. Electrochemie*, **4**, *118*; *Wied. Ann.* **62**, *425* (*1897*). The author attributes the changes in the color of the alkaline halids, under the influence of cathode rays, to the formation of new modifications. The solubility of the yellow sodium chlorid seemed to be the same as that of the unchanged salt. *W. D. B.*

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