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CONTENTS OF VOLUME IV

1. JANUARY

2. FEBRUARY

3. MARCH

4. APRIL

ON THE INVERSION OF THE HEPTA- AND HEXA-HYDRATES OF ZINC SULPHATE IN THE CLARK CELL

BY H. T. BARNES

The change in the hydration of zinc sulphate,

$$ZnSO_4.7H_2O \rightleftharpoons ZnSO_4.6H_2O + H_2O,$$

which occurs at about 39°, has been the subject of considerable investigation not only in the earlier work of E. Wiedemann,[1] but more completely in the important researches of E. Cohen.[2] During the course of an extended series of experiments which the writer undertook, with Prof. H. L. Callendar, some time ago on a study of the Clark cell, it was shown for the first time how the E. M. F. of such a cell, being a function of the solubility of the soluble electrolyte ($ZnSO_4$) as well as of the temperature, could be made to show a change of hydration by a sudden change in the E. M. F. The results of this work on the change of E. M. F. with temperature in the neighborhood of 39°, were only partially given in the original paper,[3] but as on recalculation they appear to be exceedingly consistent and steady, it was thought desirable to give them here in full. The observations were made in April, 1896, but it was not until more than a year after this that they were partially published. Since then the stress of other work has delayed the final publication. In the meantime a paper by W. Jaeger[4] was published which

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[1] Wied. Ann. 17, 572 (1882).

[2] Zeit. phys. Chem. 14, 53 (1894).

[3] H. L. Callendar and H. T. Barnes. Proc. Roy. Soc. 62, 150 (1897).

[4] Wied. Ann. 63, 354 (1897).

brought out the essential points in the measurement of the change of hydration by the change in E. M. F. of a Clark cell, with many interesting photographic reproductions of the state of the zinc sulphate solution in the stable and metastable state. As Jaeger's paper was published so soon after, and as he does not refer to the author's work, it is probable he was unaware of the experiments described there, which were on the same lines as his own. The writer's work was undertaken primarily to obtain a more accurate expression for the change of E. M. F. with temperature, and it was while studying to what extent this expression, deduced between 0° and 30°, could be relied on at the higher points, that the sudden break in the curve was noted.

The best known and most reliable electrochemical combinations for producing a constant E. M. F. are

Hg	Hg_2SO_4	$ZnSO_4$	Zn	(Clark)
Hg	Hg_2SO_4	$CdSO_4$	Cd	(Weston)

These have been studied in almost every detail, and it has been shown that the latter has a great advantage in having a much smaller temperature coefficient. Although small, the change of the Weston cell is probably greater than was at first supposed, and an anomalous change at about 15° makes any simple formula uncertain below that point. On the contrary the change of E. M. F. with temperature of the Clark cell has been shown to be exceedingly regular, and with suitable care in the construction, purification of the materials, and temperature measurements, an order of accuracy of two or three hundredths of a millivolt may be obtained between 0° and 30°. In the writer's paper above cited, this was clearly pointed out, although it seems to have been misunderstood,[1] and the accuracy obtained on reproducing the cells confused with the accuracy obtained on a change of temperature, which is quite another matter. It is not proposed at this time to say anything further in regard to the Weston cell, reserving that for a later paper. From the results of certain of the writer's experiments, however, the break in the temperature coefficient curve, which was suggested by

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[1] K. Kahle. Wied. Ann. 64, 92 (1898).

Jaeger and Wachsmuth[1] to occur at about 5°, and subsequently shown by Kohnstamm and Cohen[2] to occur at 15°, is clearly shown to occur at about 15°, although by no means as sharply defined as in the case of the Clark cell at 39°. It is probable that the change in the Weston cell is not due to a change in the water of crystallization, but to a change in crystalline form, as was suggested by Kohnstamm and Cohen.[3]

Form of Clark Cell as a Transition Cell

The three types of transition cells studied by van 't Hoff, Cohen, and Bredig are already too well known to be more than mentioned here. Cohen has termed a form of cell such as the Clark, a transition cell of the fourth type,[4] and of these four cells, the last appears to be the easiest of construction and manipulation. The form of Clark cell originally adopted by the writer, and used in obtaining the measurements about to be described, consisted of a long test-tube as containing vessel, with pure vacuum distilled mercury in the bottom for positive electrode. Carefully washed mercurous sulphate saturated with zinc sulphate, forming a paste, was placed over the mercury surface and moist zinc sulphate crystals were placed over the paste. An amalgamated pure zinc rod, immersed in the damp crystals, formed the negative electrode. A platinum wire, protected from all the ingredients of the cell except the mercury, by a glass tube, passed up through the cell and through a cork used to close the cell, to the top of the test-tube where the glass was fused around the wire in such a way as to form a mercury cup. A similar platinum wire, enclosed in a glass tube, was fastened to the zinc and passed through the cork to the top of the test-tube where a mercury cup was made, as in the positive electrode. The cell was sealed by melting marine glue over the cork. The complete cell occupied about a third of the test-tube. This, of course, is a simple modification of the Clark cell recommended by

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[1] Wied. Ann. 59, 575 (1896).
[2] Ibid. 65, 344 (1898).
[3] l. c. 356.
[4] Zeit. phys. Chem. 25, 300 (1898).

the English Board of Trade, and has been known as the B. O. T. "Crystal" cell. It will be referred to after in this paper as the test-tube form. The form of cell known as the "Inverted" cell[1] was not devised until after these experiments, so that it was not tried as a transition cell, although it would work equally well. It would probably follow a temperature change even more rapidly than the the B. O. T crystal cell, for, having the negative electrode (zinc amalgam) at the bottom of the test-tube, it is more sensitive. A sudden and sharp change of temperature causes the E. M. F. of such a cell to change considerably more than it should, after which it quickly approaches its true value as the ingredients of the cell assume the temperature of the amalgam. Another form of hermetically sealed cell used in these experiments is more difficult of construction, but from its compact shape is preferable to any type yet devised. This cell will be referred to after as the sealed cell. It is hoped a complete description of this cell may be published shortly.

Electrical Measurements

The greatest possible care was exercised in making the electrical measurements. The Poggendorff method with a 6000 ohm Thomson galvanometer was used for comparing the cells. The potentiometer consisted of a platinum silver wire two meters long, in half meter lengths, placed side by side and connected between two very accurate 2000 ohm resistance boxes. The wire had a millimeter scale and sliding contact piece with two contacts for each wire, one on either side of the slider. This made it possible to work close up to the ends of the wires, and to have a very steady, strong slider. If r is the resistance of the wire and l the total length, then in order to have the readings of the potentiometer direct in millivolts, 1 mm to 0.01 mv, it was necessary to have the potential drop across $l = 20$ mv, and resistance of first box $= R_1 = \frac{Er}{20}$, E being the potential drop in mv most convenient between the terminals of the first box. The resistance of the second box R_2 is calculated by

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[1] Electrician, 39, 638 (1897); 40, 165 (1897).

knowing approximately the E. M. F. of the accumulator supplying the steady current for the potentiometer. Where E is in mv as before and e is the E. M. F. of the accumulator also in mv, then

$$R_2 = \frac{(e - E + 20)r}{20}.$$

Instead of knowing e accurately it is easier to calculate R_2 approximately and then adjust until the balance point of a Clark cell at 15° comes to a point on the wire corresponding to its value at that temperature. Having once set the bridge and determined $R_1 + R_2$, large changes in E. M. F., greater than can be measured on the bridge wire, are measured by increasing or decreasing R_1 by an amount ΔR provided R_2 is also decreased or increased ΔR, keeping always $R_1 + R_2$ constant. Equivalent length of bridge wire corresponding to ΔR may be easily calculated or best directly determined. It is convenient for adjustment to a Clark cell at 15° to make $E = 1420$ millivolts. Special care was taken to avoid defective insulation. The bridge wire was also carefully tested for uniformity.

Temperature Measurements

Two water-baths were constructed and arranged with thermoregulators. One of these baths was kept throughout the experiments constantly at 15°, while the other was set to regulate at any desired point up to 50°. Both baths were capable of regulating to 1/20 of a degree at any point between these limits. The form of regulator which was found to give the best results is that described by Ostwald in his "Physico-Chemical Measurements,"[1] as due to D'Arsonval. In this the expansion of the mercury, contained in the bulb alone or with alcohol or toluene, extends a rubber membrane which closes the open end of a glass tube, thereby cutting off the gas supply flowing through. It is found better to use a platinum or light copper disk between the rubber and inflowing gas to give a sharper cut-off. The chief advantage of this regulator is that the mercury

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[1] English translation, p. 61, Fig. 44 (1894).

surface forming the cut-off never becomes fouled by the gas. After considerable experience with other forms of gas regulators this form is beyond compare, and with a sufficiently large bulb, about 100 cc. for alcohol or toluene and proportionally larger for mercury, regulation to 1/100 of a degree can be attained with a minimum amount of trouble.

The great length of containing vessel for the forms of cells used in these experiments made it possible to deeply immerse the cell. This is of considerable importance at higher points, especially in the test-tube form where the zinc rod is at the top and capable of conducting heat rapidly away from the interior of the cell. This cannot occur in the sealed type. The method of bringing the electrodes out of the top of the cell made it possible to be free from any defective insulation. Needless to say the importance of very vigorous stirring was not overlooked, and special stirrers, run by a water-motor, were indispensable parts of the baths. The temperature was read by means of a Geissler thermometer graduated to 1/10 of a degree, which had been repeatedly calibrated by means of a platinum thermometer. When the Geissler was in use in the hot bath the constancy of the 15° bath was watched by means of a Hicks' thermometer reading 1 mm to 1/10°.

Method of Making the Experiments

The method of taking the first set of readings to determine the shape of the E. M. F. temperature curve above 30°, was to have one of the baths regulating at 15° and the other regulating at the desired temperature. Comparisons were made on a number of cells in the cold bath, after which the cells to be investigated were transferred to the hot bath. One cell was always left in the cold bath to check the constancy of the accumulator. Readings were then made at intervals, and after about an hour or two the cells were transferred back to the cold bath. As a rule the cells assumed their final values after only about 10 or 15 minutes' immersion. The state of moisture of the zinc sulphate crystals appeared to determine the speed with which they assumed their steady values. Cells made with very dry crystals appear to take longer to change, hence it is essential to have the crystals sufficiently moist. The difference, however, is only slight. The observations were expressed as difference in millivolts between the readings at 15° and those at the higher points, correcting for small changes in temperature, if any, of the cold bath and changes in bridge reading, due to the accumulator. By tests made in this way at intervals between 30° and 50° it was clearly seen that a break occurred in the temperature curve. In order to find out at just what point the change took place from one curve to the other, one series of ascending and two series of descending readings were taken. To do this the cold bath was kept constantly at 15° and the hot bath very slowly heated, by disconnecting the regulator, from a point about 39° to a point several degrees above. During this time readings were made every few minutes of the E. M. F. and temperature, and frequent readings on a cell kept in the cold bath. For the descending series the hot bath was allowed to cool down slowly, and similar readings taken as for the ascending series. In both cases the E. M. F. was carried considerably beyond the transition point into the metastable region. For the ascending series the change in phase occurred much sooner, as would be expected, than for the descending series. In both cases the temperature of the bath was changed so slowly that the temperature of the cells could not have lagged more than a very small fraction of a degree behind the bath.

Experimental Results

The first set of results for the higher points have already been published.[1] They are reproduced here in Table I for the sake of comparison.

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[1] l. c., p. 149.

TABLE I

Temp C	Observed change in mv from 15° C	Calculated by linear formula	Difference
40.60	—35.81	—30.72	—5.09
30.14	19.78	18.17	1.61
30.32	20.00	18.38	1.62
35.44	27.39	24.53	2.86
42.58	36.56	33.10	3.46
46.74	41.14	38.09	3.05
48.58	43.50	40.30	3.20
35.79	28.08	24.95	3.13
40.09	34.99	30.11	4.88
42.79	36.76	33.35	3.41
44.70	38.88	35.64	3.24
41.54	35.45	31.85	3.60

The method of expressing these and subsequent results is to assume the linear expression

$$E_t - E_{15^\circ} = - 1.200\,(t - 15)$$

and difference the observed change between t° and 15° from that calculated by this expression, which represents very nearly the average change in millivolts per degree between 0° and 30°. This gives the most effective way of showing the results graphically. Table II gives the ascending series for the test-tube form (Cell X_3).[1] Table III gives a descending series for the same cell. Tables IV and V give the corresponding ascending and descending series for the sealed form (Cell S_4). Tables VI and VII give the second descending series for the same two cells, but was taken several days after the first set. These readings were made in order to observe more clearly the change of the hexahydrate into the heptahydrate, which occurs at about 30° for these cells. For the first set unfortunately no readings were obtained during this change, but a comparison of the cells at 15° showed that they had been completely transformed. Graphically the results are represented in Fig. 1. The plot is vertical scale difference in millivolts from linear formula, and horizontal scale temperature in centigrade degrees. The arrows show the way in which the ascending and descending series

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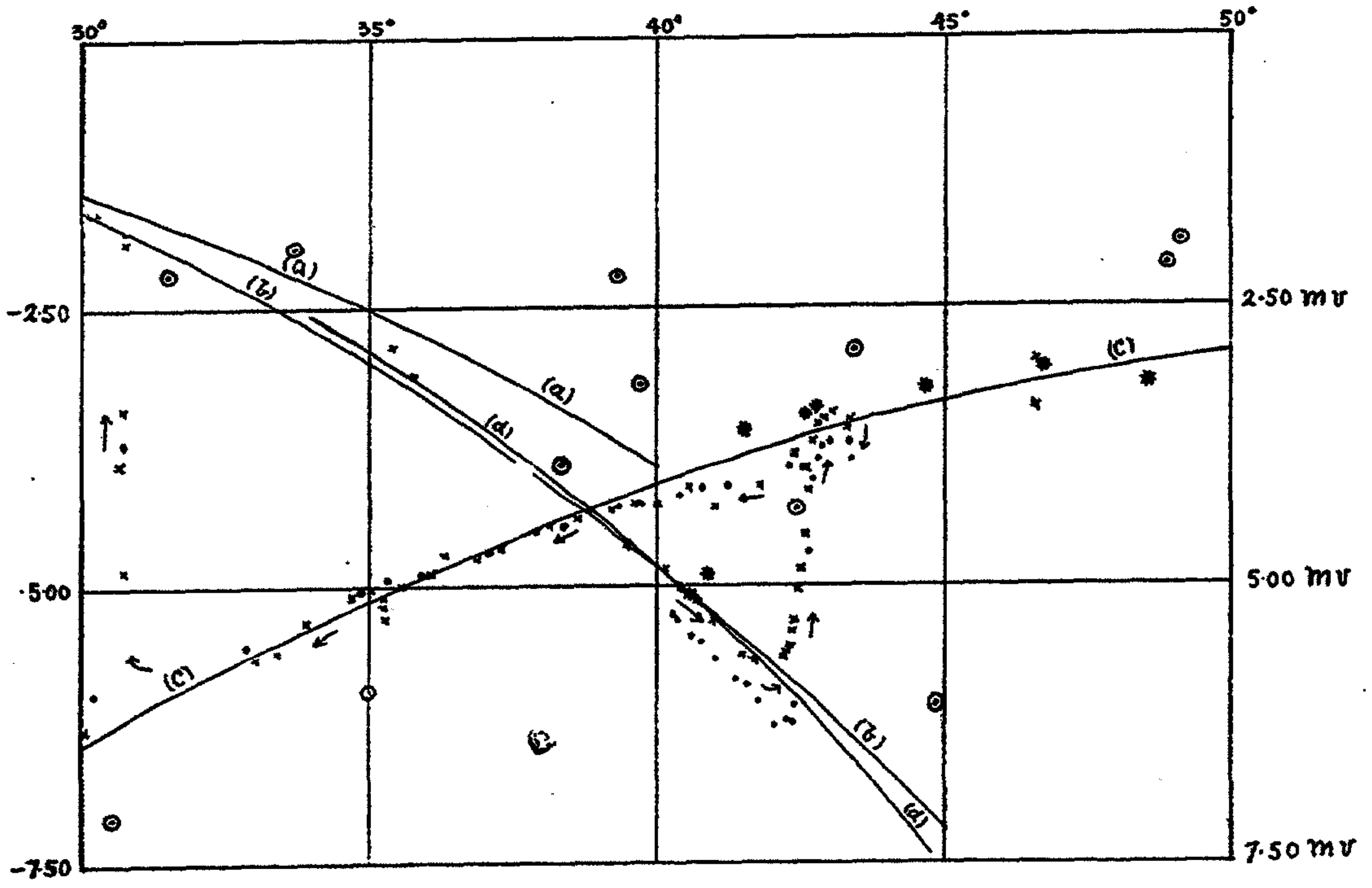
[1] l. c. p. 151.


30°
35°
40°
45°
50°
-2.50
-5.00
-7.50
2.50 mV
5.00 mV
7.50 mV
(a)
(b)
(c)
(d)

were made. The crosses show the results for the test-tube form, while the dots show the results for the sealed form. It will be noted that at about 42° in both cells the change from the heptahydrate to the hexahydrate branch took place on the ascending series, and that on the descending the change took place at about 30°. On the ascending branch the sealed type lies somewhat below the test-tube form, but it is probably not due to the lag of the temperature of the larger cell behind the temperature of the

TABLE II

April 13, 1896

Clark Cell Inversion. Test-tube Form

Temperature rising			
Time	Temp.	Total change in mv. from 15°	Difference from value calculated by linear formula — 1.20(t − 15°)
4.29	39.48°	−34.01	−4.63
7.36	39.46	34.17	4.82
7.53	40.12	35.03	4.89
8.01	40.39	35.50	5.03
8.16	40.71	36.01	5.16
8.27	40.98	36.50	5.33
8.47	41.49	37.35	5.56
8.58	41.73	37.77	5.70
9.27	42.25	38.42	5.72
9.30	42.28	38.37	5.64
9.33	42.31	38.32	5.55
9.35	42.37	38.26	5.42
9.38	42.40	38.19	5.31
9.44	42.46	37.98	5.03
9.46	42.49	37.86	4.87
9.50	42.57	37.62	4.54
9.56	42.66	37.32	4.13
9.59	42.68	37.18	3.97
10.05	42.73	37.00	3.73
10.12	42.78	36.93	3.60
10.14	42.81	36.92	3.55
10.18	42.87	36.97	3.55
10.21	42.91	37.01	3.52
10.27	43.06	37.13	3.46
10.35	43.17	37.24	3.44
10.51	43.38	37.46	3.53

TABLE III

April 14, 1896

Clark Cell Inversion. Test-tube Form

Temperature falling

Time	Temp.	Total change in mv. from 15°	Difference from value calculated by linear formula $-1.20(t-15^\circ)$
9.43	43.31	—37.58	—3.61
10.01	43.31	37.59	3.62
10.19	42.52	36.94	3.92
10.26	42.39	36.68	3.81
10.37	41.82	36.29	4.11
10.50	41.53	35.76	3.93
11.00	41.17	35.47	4.07
11.22	40.57	34.79	4.11
11.33	40.30	34.50	4.14
11.47	40.01	34.27	4.26
12.00	39.62	33.79	4.25
12.15	39.22	33.34	4.28
12.22	39.07	33.20	4.32
12.47	38.60	32.71	4.39
1.06	38.16	32.25	4.46
1.35	37.30	31.41	4.65
1.45	36.91	31.03	4.74
2.36	36.33	30.25	4.66
2.49	36.08	30.16	4.87
3.08	35.56	29.66	4.99
3.31	35.03	29.04	5.01
3.46	34.71	28.74	5.09
3.47	34.69	28.68	5.05
3.51	34.57	28.56	5.08
4.15	33.94	28.06	5.33
4.18	33.40	27.69	5.61
4.27	33.04	27.32	5.67
4.37	30.04	24.35	6.30
4.55	15.43	0.77	0.24

TABLE IV

April 13, 1896

Clark Cell Inversion. Sealed Form

Temperature rising

Time	Temp.	Total change in mv. from 15°	Difference from value calculated by linear formula $-1.20(t-15^{\circ})$
4.30	39.48	−34.28	−4.90
7.36	39.46	34.31	4.96
7.57	40.25	35.56	5.26
7.59	40.33	35.69	5.30
8.09	40.57	36.13	5.45
8.18	40.76	36.43	5.52
8.28	41.01	36.90	5.69
8.40	41.34	37.47	5.86
8.49	41.54	37.78	5.93
8.59	41.76	38.20	6.09
9.15	42.06	38.75	6.28
9.28	42.26	39.04	6.23
9.34	42.35	39.09	6.27
9.39	42.41	39.02	6.13
9.47	42.52	38.68	5.66
9.57	42.66	37.88	4.69
10.06	42.74	37.35	4.06
10.15	42.84	37.25	3.84
10.22	42.94	37.28	3.75
10.36	43.18	37.53	3.72
10.52	43.38	37.77	3.72

TABLE V

April 14, 1896

Clark Cell Inversion. Sealed Form

Temperature falling			
Time	Temp.	Total change in mv. from 15°	Difference from value calculated by linear formula $-1.20\,(t-15^\circ)$
9.45	43.36	−37.87	−3.84
10.03	43.33	37.77	3.78
10.17	42.56	37.01	3.94
10.31	42.31	36.69	3.92
10.39	41.76	36.17	4.06
10.57	41.26	35.60	4.09
11.14	40.79	35.07	4.12
11.28	40.42	34.68	4.18
11.55	39.76	33.96	4.25
12.11	39.31	33.46	4.29
12.35	38.85	32.95	4.33
12.50	38.42	32.54	4.44
1.15	37.94	32.04	4.51
1.40	37.10	31.20	4.68
2.37	36.31	30.27	4.70
2.45	36.16	30.23	4.84
2.55	35.97	30.06	4.90
2.58	35.86	29.94	4.91
3.37	34.89	28.91	5.04
4.28	32.89	27.01	5.54
4.38	30.16	24.18	5.99
4.56	15.43	0.70	0.17

TABLE VI

April 28, 1896

Temperature Falling

Test-tube form			
Time	Temp.	Total change in mv. from 15°	Difference from value calculated by linear formula $-1.20\,(t - 15^\circ)$
4.31 (27th)	46.62	—40.92	—2.98
9.46 (28th)	46.65	41.40	3.42
10.17	41.00	35.52	4.32
10.19	40.97	35.49	4.33
11.00	35.28	29.63	5.30
11.07	35.29	29.54	5.19
11.18	35.29	29.47	5.12
12.02	30.74	23.74	4.85
12.16	30.68	22.71	3.89
12.22	30.75	22.33	3.43
2.43	30.76	20.79	1.88
5.09	14.95	0.03	0.09

TABLE VII

April 28, 1896

Temperature falling

Sealed form			
Time	Temp.	Total change in mv. from 15°	Difference from value calculated by linear formula $-1.20\,(t - 15^\circ)$
4.30	46.65	—41.48	—3.50
9.47	46.63	41.60	3.65
10.18	41.00	35.25	4.05
11.01	35.29	29.28	4.93
11.19	35.29	29.28	4.93
12.03	30.75	23.90	5.00
12.20	30.76	22.64	3.73
2.44	30.76	20.68	1.77
5.10	14.95	+0.16	+0.10

bath, but to another cause which will be discussed later. This is also associated with the fact that the earlier results, given in Table I, and marked on the plot with double crosses, lie above those for the later results.

The expression connecting the E. M. F. with temperature, which was found to fit the observations most closely between 0° and 30° is in millivolts

$$E_t - E_{15^\circ} = -1.200\,(t - 15^\circ) - 0.0062\,(t - 15^\circ)^2 \ldots\ldots (a)$$[1]

and is shown in the figure by plotting the second term. The observations at 30° diverge a little from this simple parabolic expression, and those above considerably more, as has been clearly pointed out in another place.[2] By introducing a third term

$$-0.00006\,(t - 15^\circ)^3 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (b)$$

formula *a* is brought into closer agreement with the observation above 30°. The complete expression which will be found to fit very accurately between 15° and 40° may read

$$E_t - E_{15^\circ} = -1.200(t - 15^\circ) - 0.0062\,(t - 15^\circ)^2 - 0.00006(t - 15^\circ)^3.$$

Below 15° the simple parabolic formula *a* is most accurate. It will be seen that to extrapolate from formula *a* for a mean temperature of 39° would give quite an erroneous result. Even taking formula *b*, the observed change is larger between 35° and 42° if full weight be given to the observations at 35° which lie a little above *b*. For a mean temperature of 39° the following simple expression fits the results fairly well

$$E_t - E_{39^\circ} = -1.635\,(t - 39^\circ) - 0.0140\,(t - 39^\circ)^2 \ldots\ldots (d)$$

The expression for the hexahydrate branch may be given

$$E_t - E_{39^\circ} = -1.000\,(t - 39^\circ) - 0.007\,(t - 39^\circ)^2 \ldots\ldots (c)$$

Although these are worked out for a mean temperature of 39°, yet it is clear that the point of transition given by the observations lies a little below this temperature. The total change between 15° and 39° for a cell on the heptahydrate branch is very

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[1] l. c. p. 132.

[2] l. c. p. 132.

nearly — 33.23 mv, while that for a cell on the hexahydrate branch is — 33.10 mv. This gives a difference at 39° of 0.13 mv, which corresponds to a lowering of the point of transition 0.22°. This gives the point of actual crossing of the two branches of the curve 38.78° C.

Results of Jaeger

For the sake of comparison Jaeger's observations have been reduced on the same plan and shown within the limits of the plot by circled dots. His method of measurement consisted in enclosing a Clark cell of the H-form, recommended by Kahle, in a paraffin bath, which was in turn enclosed in a water-bath, the temperature of which he could change at will. Comparisons were made of the E. M. F. of the Clark cell with that of a Weston cell, kept at about 20°. The results of the direct comparison are expressed in volts, giving the absolute value of the Clark cell at any temperature, assuming that at 15° to be 1.4330 volts. The E. M. F. of the Weston at 20°, by direct comparison with a Clark cell at 15°, was taken as 1.0190 volts. In Table VIII the results are expressed in millivolts, as in the other tables. The differences from the linear formula are given in the fifth column and plotted in the figure.

TABLE VIII

Jaeger's Observations on the Inversion of the Hepta- and Hexahydrates of $ZnSO_4$ between 30° and 50°

Temp	E. M. F.	Difference in mv from cell at 15°	$- 1.20(t - 15°)$	Difference
31.5	1.4110	—22.0	—19.8	-2.2
38.3	1.4011	31.9	28.0	3.9
43.4	1.3960	37.0	34.1	2.9
49.1	1.3902	42.8	40.9	1.9
38.0	1.3990	34.0	27.6	6.4
35.0	1.4030	30.0	24.0	6.0
30.5	1.4073	25.7	18.6	7.1
33.7	1.4086	24.4	22.4	2.0
39.3	1.4016	31.4	29.2	2.2
39.7	1.4002	32.8	29.6	3.2
42.4	1.3958	37.2	32.9	4.3
44.9	1.3910	42.0	35.9	6.1
48.9	1.3902	42.8	40.7	2.1

The general indication of the results is the same as the writer's, but the point of transition is not clearly marked. Instead of deducing the temperature expression for a mean temperature of 39° from his observations, an extrapolated expression from Kahle's formula between 0° and 30° is given. Kahle's expression, which stands in remarkable agreement with formula *a*, is

$$E_t - E_{15^\circ} = -1.19(t - 15^\circ) - 0.007(t - 15^\circ)^2.$$ [1]

The extrapolated formula given by Jaeger is

$$E_t - E_{39^\circ} = -1.52(t - 39^\circ) - 0.007(t - 39^\circ)^2.$$

It was pointed out before that such an expression would not represent the results accurately. Not only does it make the average change per degree about the mean temperature of 39° too small, but it also assumes the rate of change to be the same at the higher points. As a matter of fact the rate of change is just double that given by Jaeger. For the hexahydrate branch, which was deduced from his observations, Jaeger gives

$$E_t - E_{39^\circ} = -1.02(t - 39^\circ) - 0.004(t - 39^\circ)^2.$$

This is in good agreement with formula *c*. Although not shown in Table VIII, it is seen by reference to Jaeger's observations that he was able to preserve the hexahydrate as metastable phase as low as 0°. In both cases the author was unable to measure the abnormal curve below 30°. It was a well known fact that cells kept at a high temperature on returning remained in an abnormal condition at the lower points until a crystal of the normal salt was introduced.[2] But this was noted for the old form of Board of Trade cell with saturated solution and few crystals. In Jaeger's cells the $ZnSO_4$ solution was in excess, while in the cells used by the writer the crystals were in excess, there being just enough solution to keep them moist. This seems a strong argument in favor of the B. O. T. "Crystal" cell, for although it was kept twice above 40° all night, and had shown by its E. M. F. that it had become completely transformed, yet

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[1] Zeit. Instrumentenkunde, 17, 143 (1897).

[2] Rayleigh. Phil. Trans. 176, 788 (1885).

in both trials it refused to remain in an abnormal condition below 30°.

Secondary Change above 35° C.

It seems likely that a cell undergoes a secondary change above 35°, due to the decomposition of the mercurous sulphate. Taking a cell such as the test-tube form and heating it above 40° long after the cell has assumed the temperature of the bath, a slow drop in the E. M. F. takes place. This is shown most markedly in Tables VI and VII. About one hour after immersing cell X_3 at 46.62° it showed a total drop in its value from 15° of 40.92 millivolts. The next morning after remaining all night at 46°, the value had changed to 41.40, a difference of nearly half a millivolt. A similar change, though smaller, was noted on the sealed cell. The first value given by the test-tube form agrees well with those in Table I, which stand higher on the plot than the two descending series. Moreover in the ascending series when the change from one branch of the curve to the other occurs at 42° the E. M. F. rises to a point higher than it reaches five or six hours later. This secondary change serves to explain why the smaller sealed cell, which contains much less of the ingredients, lies below the test-tube form on the ascending series, and when the change occurs does not rise so high nor subsequently change so much as the test-tube form, and finally why both cells pass back along the same path on the descending series. It seems probable that this change is the cause for the more rapid falling off in the E. M. F. temperature curve above 30°. Whatever the change is, if it is due to the decomposition of the mercurous sulphate, it does not effect the value of the E. M. F. at the lower points.

Associated with this it is interesting to mention here an effect noted by the writer in the preparation of the crystals of $ZnSO_4$ for the "Crystal" cell. The method adopted is to prepare a saturated solution of $ZnSO_4$ at about 30°, and after treating with a small quantity of washed mercurous sulphate in the usual way and filtering at 30° the solution is cooled to 0°, and the supernatant liquid poured off from the batch of crystals produced. It has been noticed that if the temperature of the solution containing the Hg_2SO_4 rises to 35° or over, that on cooling a yellow turbidity appears, which does not appear where the temperature of the solution does not rise above 30°. This may be associated with the more rapid falling off in the temperature curve for the higher points, but requires further investigation.

Inversion Point as Measured by the Solubility of the Hepta- and Hexahydrates of $ZnSO_4$

A careful study of the change of solubility of zinc sulphate with temperature shows, as would be expected, a sudden break in the curve at the inversion point of one hydrate into the other. As was pointed out by Cohen,[1] a considerable discrepancy appears here of over a degree from the point deduced by the electrical measurements. In Table IX the writer's solubility determinations between 0° and 50° are reproduced. The weight of salt p is here expressed in percent of solution.

TABLE IX

Solubility of the Hepta- and Hexahydrates of $ZnSO_4$

Temp	p observed	p calculated from formula 1	p calculated from formula 2
0°	29.43	29.50	....
0	29.53	29.50	....
0	29.49	29.50	....
15.00	33.66	33.70	....
15.88	33.85	33.95	....
30.70	38.46	38.44	....
39.92	41.36	41.32	41.33
39.95	41.37	41.34	41.34
40.73	41.43	....	41.49
41.49	41.70	....	41.65
46.40	42.68	....	42.71
49.97	43.51	....	43.50
49.99	43.41	....	43.51
50.00	43.50	....	43.51
50.02	43.51	....	43.52

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[1] Zeit. für phys. Chem. 25, 304 (1898).

The formula representing the change of solubility between 0° and 39° is

$$p = 29.5 + 0.270\,t + 0.00068\,t^2 \ldots\ldots\ldots\ldots (1)$$

while the expression for the hexahydrate from 40° may be given

$$p = 41.35 + 0.210\,t + 0.00070\,t^2 \ldots\ldots\ldots\ldots (2)$$

In the table p calculated by formula 1 is given in the third column, and by formula 2 in the fourth. It will be seen that at about 39.95° the solubilities become equal. This discrepancy in the two results is probably not real, but the explanation is to be looked for in the lowering of the inversion point in the Clark cell by the presence of the mercurous sulfate.

No mention has been made in this paper to the temperature "lag" which has for so long a time been a subject of such repeated investigation by Clark cell observers. This effect, which renders the old form of Board of Trade cell so unsuitable for accurate work, has been not only completely explained, but entirely done away with, and may be considered, without reserve, entirely out of account in the present experiments.

McGill University, Nov. 23, 1899

THE MELTING-POINT OF CHLORAL HYDRATE

BY C. G. L. WOLF

In a series of papers on evaporation and dissociation, Ramsay and Young have examined the behavior of chloral hydrate on heating and observed that this substance can be heated under reduced pressure to 64° without melting. Naumann[1] and others have also shown the very complete dissociation which takes place in the vapor phase. As the melting-points of this substance have been given as ranging from 48° to 57°, it has been thought advisable to examine this point more closely as it is possible that the variations observed may not be due to errors of observation, but to the changes which take place in the substance on heating.[2]

If one take as a general case a compound AB, made up of two components A and B, one may express the change in melting-point consequent on dissociation of the compound by the concentration-temperature diagram (Fig. 1).

The point C will then represent the melting-point of the pure compound when there is no dissociation. Should dissociation take place, the freezing-point is lowered and C_1 will represent the temperature at which the solid compound is in stable equilibrium with a melt containing both dissociation products A and B. Should dissociation take place, C is depressed and one gets a lower freezing-point. C will then represent the melting-point of the pure compound when no dissociation takes place. C_1 will represent a melting-point corresponding to a certain amount of dissociation which takes place at the temperature represented by a coordinate cutting the point C_1.

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[1] Naumann. Ber. chem. Ges. Berlin, 10, 822 (1877); Würtz. Comptes rendus, 84, 971 (1877); 88, 825 and 861 (1879); 90, 98 (1880).

[2] Cf. Bancroft. Jour. Phys. Chem. 3, 85 (1898).

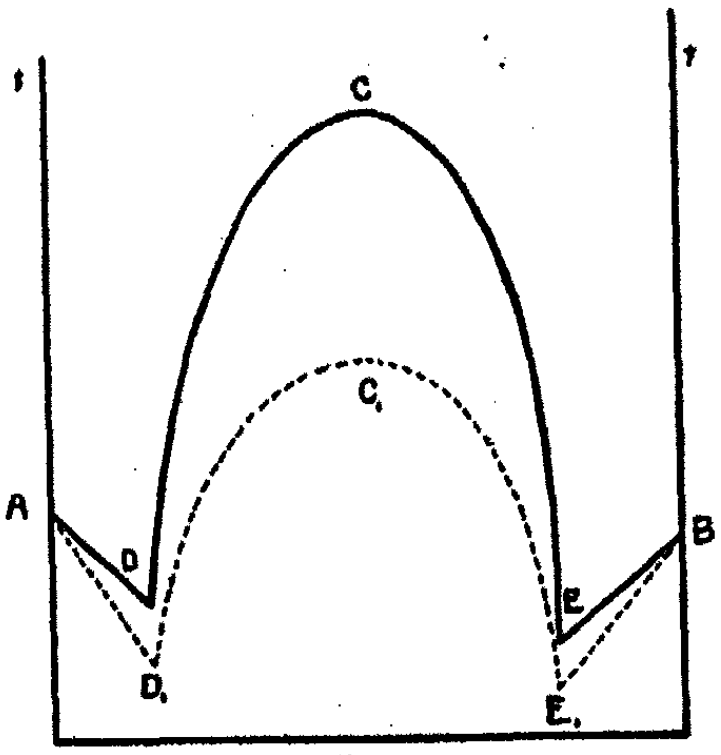

Fig. 1

Melting-points between C and C_1 could be realized in the case of a substance which dissociates with measurable slowness. If the compound be heated up to its melting-point and be allowed to cool rapidly, the amount of dissociation would be small and one would therefore expect to obtain a freezing-point comparatively near the original melting-point. Were the substance cooled sufficiently slowly so as to allow the dissociation to proceed far, then on heating again one would obtain a melting-point lying much lower on the temperature axis. On the other hand, could one remove the product of dissociation rapidly enough, one should arrive at the true melting-point of the substance, providing a sublimation temperature was not reached first.

Ramsay and Young in their experiments on the vapor pressure of chloral hydrate, heated this substance which had been previously fused on the bulb of a thermometer in a vacuum, and observed that no melting took place at 64°, although at atmospheric pressure the identical crystals melted at 50.6°. This could be explained by assuming that under these conditions the products of dissociation were removed with such rapidity that no point on a line joining C and C_1 was realized. When however the pressure was raised sufficiently, the substance melted and fused at once. Here one was obviously dealing with a system containing a compound and one or both of the components, with a consequent lowering of the melting-point below that of the true fusion of the undissociated substance.

On the other hand, chloral hydrate has been assumed to contain two substances whose formulæ have been variously given and should one, on heating, really deal with two isomeric modifications in the melt, together with the products of dissociation, one would then have to do with a system more complex than the foregoing, and which could be represented schematically as follows:

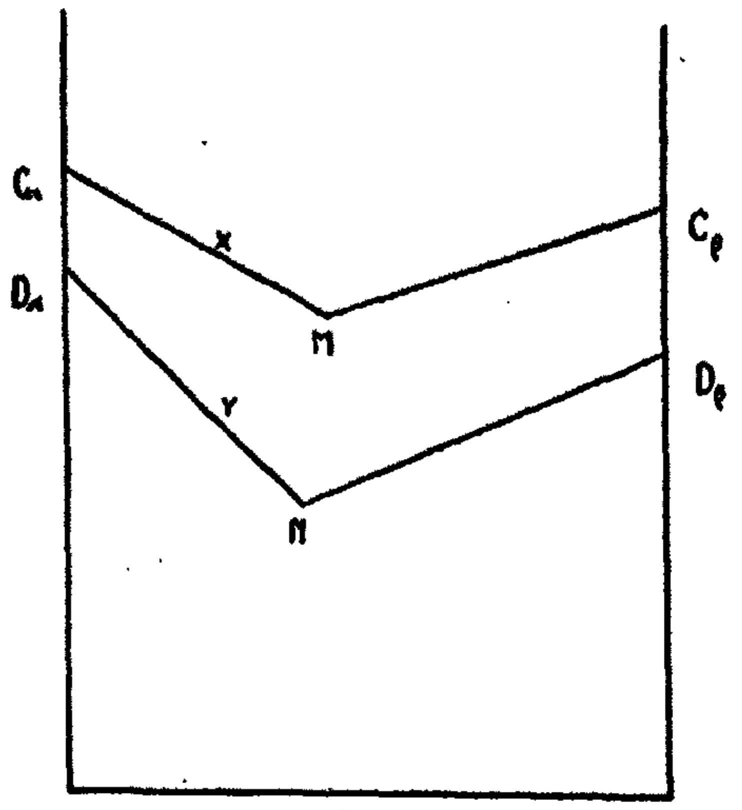

Fig. 2

Let C_α and C_β represent the melting-points of the two modifications and D_α and D_β the melting-points of the two isomers, lowered by the presence of the products of dissociation. Then to each of the compounds, the temperature between C_α and C_β would correspond to a line joining C and C_1 on the preceding diagram. If C_α were the more stable, and it could be proven that no dissociation took place, but simply that a change of C_β into C_α took place, then one would obtain a stable freezing-point on melting and cooling either isomer, represented by X where the one form as solid phase was in stable equilibrium with solution and vapor. On the other hand, did dissociation accompany this change into the stable form, one would get a further fall of the freezing-point corresponding to point Y on the curve $D_\alpha YN$, where the one form in solid phase was in equilibrium with the dissociation products and the isomers as liquid phase. M would be a point where C_α and C_β would coexist as solid phases with liquid and vapor, and N where the components C_α and C_β would coexist with the dissociated liquid and vapor. Hence, to put the case more concretely, did one have a compound existing in two modifications, one might have the following phenomena taking place.

I. On obtaining the two isomers and heating rapidly, or in some other way inhibiting the amount of dissociation, one would obtain high melting-points corresponding respectively to C_α and C_β. Did dissociation simultaneously take place, one would obtain various melting-points between C_α and D_α, and C_β and D_β.

II. Did no dissociation take place, but simply tautomeric change, one would obtain on long heating a melting-point corresponding in temperature and in the relative concentration of the two forms to a point on the curve $C_\alpha MC_\beta$.

III. With the two changes described as I and II taking place at the same time, viz., Tautomerism and Dissociation, one gets final equilibrium at Y on the curve D_α and ND_α.

In order to arrive at a conclusion regarding the changes which take place on heating, it would therefore be necessary to heat the compound or compounds under as many conditions as would favor or retard both changes and dissociation, and further, to perform the experiments in such ways as could bring together desired combinations of the two processes.

The chloral hydrate used for these experiments was commercial. The substance was in large transparent plates. Experiments made in this laboratory in the previous winter on the purification of the substance by fractional crystallization from chloroform, carbon disulphide, chloral, water and other solvents, led to unsatisfactory results, as the melting-point of the successive products varied irregularly within limits of two or three degrees. The preparation of the hydrate from chloral and water also gave a product which did not differ from the substance on hand, so that eventually it was decided to use the commercial article without further purification. The substance, moreover, satisfied all the requirements of pure chloral hydrate.

The experiments of Ramsay and Young[1] were repeated and the apparatus used was essentially the same as that used in their earlier experiments.[2] The pressure was measured by a differential manometer instead of barometer and cathetometer, exhaustion being effected by a water-pump. The **H** form of the tube was found useful as duplicate experiments could be made under identical conditions. The tube was heated in a water-bath, the temperature of which was varied from 80° to 100°. The temperature of the bath had apparently no effect on the final results. The thermometer bulbs were coated with chloral hydrate by immersing in fused chloral hydrate cooled nearly to the solidification point, and the length of time after coating was noted. In one instance, a thermometer was allowed to stand in a closed test-tube for some three weeks after coating.

It was found that when the thermometers were used shortly after coating that a slight preliminary fusion took place at 50° under a pressure of 22 mm. This appearance of rounded edges soon disappeared and the coating was then in every respect identical with that on the thermometer which had stood for twenty-four hours after coating.

The temperature of the thermometer rose slowly to 72° and remained there for some time. During this time the coating on the thermometer becomes perceptibly thinner.

If now the pressure be raised to 35 mm by the admission of air, slight fusion takes place. The thermometer drops to 69°, 70°, and if the vacuum be restored quickly enough, the mass solidifies, the temperature of the mass rising again to 72°. If, however, a large amount of air be introduced into the apparatus,

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[1] Phil. Trans. 177, I, 77 (1886).

[2] Ibid. 175, II, 471 (1884).

the substance melts instantly. In this case the thermometer drops an indefinite number of degrees according to the amount of substance remaining on the bulb.

The hydrate evaporates quickly, and the thermometer then rises and indicates a temperature nearly that of the bath. Under no circumstances could the substance be fused at 22 millimeters, so that it is safe to assume that at this pressure the sublimation point is in the neighborhood of 72°, and consequently the true melting-point of the undissociated substance must lie higher. That the temperature can be raised to this height is due either to the fact that the products of dissociation are removed so quickly that they have no time to lower the melting-point or, in case a second form be present, that one modification is removed more quickly in the vapor phase. It is more probable that the former is the case. Experimental evidence to test this view will be advanced further on in this paper.

It was thought advisable to try to reproduce these experiments, using a mass of the substance, immersing the thermometer in the crystals. To this end a number of trials were made under various conditions.

The simple apparatus consisted of a long tube provided with a side neck and jacketed by an outer tube which served as an air-bath. The inner tube contained a thermometer, the bulb of which was completely covered with crystals. This tube was connected to the water-pump and exhausted to the vapor-tension of the water, a manometer being interposed to record any change of pressure which might take place. It was found that the greater part of the hydrate sublimed off before the thermometer rose to 50°. Furthermore, the hydrate which seemed to be condensed on the side of the tube in a supercooled condition, flowed back and saturated the crystals, making it impossible to observe any preliminary melting. This was partially obviated by taking a retort of about 200 cc capacity, which was filled nearly to the angle with chloral hydrate. The neck was joined to a distilling flask, which acted as a condenser, and this, in turn, was connected with the manometer and pump. The retort was heated by a calcium chlorid bath, giving a temperature of 115°.

Numerous pressures and temperatures were tried in order to get a means by which the vapor would be removed with sufficient rapidity, and which would still admit of the substance being heated to its melting-point without too much volatilization taking place. This plan was not found to be feasible with the large amount of the substance taken. The sides of the retort were superheated to such an extent by the bath that the hydrate next the walls was completely fused before the temperature in the interior was 40°. On the other hand, if the bath were not heated high enough, sublimation took place so rapidly that a great deal of heat was extracted, more than sufficient to raise the temperature of the mass inside.

A side-necked tube, sufficiently long to contain the thermometer, was next made. Into this was introduced a paper capsule, such as is used for ether extraction. This rested on a layer of cotton wool in the bottom of the tube. The bulb of the thermometer occupied the center of the capsule surrounded by the crystals. All precautions were taken to prevent the annoying soakage effects. The tube was jacketed and heated in a water-bath to 100°. This apparatus gave equally unsatisfactory results. It is thus evident that at pressures sufficiently low to remove the vapor phase, it is impossible to heat a quantity of the hydrate uniformly throughout the mass, without volatilizing it in a comparatively short time. Whereas, if sufficient heat be supplied, either the experiment is vitiated by the reflux of supercooled hydrate or the crystals in contact with the walls are heated to a much higher temperature than those in the center of the tube. Besides, it is more than probable that the products of the dissociation which take place are removed with difficulty from the interior of a mass, and hence, remaining there, lower the melting-point of the whole enormously. On the other hand, should one of the isomers be the more volatile, it would seem to be impossible under these conditions, to remove the vapor of the one sufficiently rapidly to leave the product of but one modification at the end of the experiment.

The conditions of the Ramsay and Young experiment are therefore more favorable to success, as here one has a thin layer of substance closely adherent to the bulb of the thermometer, and absence of superheating through complete independence of the walls of the heating vessel, and of the crystals.

It was next of interest to know how, under carefully observed conditions, chloral hydrate behaves when heated alone in the ordinary way in capillary tubes and in mass, and if the presence of dissociation products or of modification would make itself evident.

Small sealed capillary tubes containing the substance were heated in the ordinary melting-point apparatus, no particular attention being paid to the rate of heating. The substance commences to soften at 48°, is incompletely fused at 51°, and completely melts at 54.1°. This may be said to be but one case for, as will be shown, the conditions under which the experiment is done, play a very great part in the results obtained. In another case, when a modification of the double-walled Anschütz flask was used, melting commenced at 49.2° and was complete at 50.6°. This latter is the temperature given by Ramsay and Young as the melting-point for the substances.[1] If the tube be cooled rapidly no crystallization takes place for some time, and indeed on standing at room temperature an hour may elapse before crystals appear, showing undoubtedly the tendency to supercooling possessed by the substance. A tube which had been melted and had stood over night gave a melting-point of 51.6°. Small crystals remained at this temperature, and these disappeared when the bath was raised to 52.6°.

Since the melting-point of the substance, as determined in the ordinary way, would point to no definite result, it was thought advisable to examine the substance in an open tube with the thermometer in the melt. These conditions were also favorable for observing the freezing-point, as supercooling could be avoided by the introduction of crystals of the substance at any convenient time. In each case the tube was jacketed to facilitate equal heating, and in most instances where the melting-

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[1] Phil. Trans. 177, I, 77 (1886).

point was observed, the bath was kept in constant motion with a stirrer.

If one heat fresh chloral hydrate slowly in an open tube in this way, preliminary melting takes place at 47.8°, at which temperature the crystal edges become rounded. At 50.6° the substance is rapidly melting and the melt is clear at 52.7° except for some few crystals which remain in the liquid in spite of vigorous agitation and keeping the liquid at this temperature for some time. The crystals persisted while the temperature was raised to 61.5°. This phenomenon is frequently observed when one has occasion to melt the hydrate, whether it has been previously fused or not.

After complete fusion was obtained the same tube was cooled and allowed to stand for some time, and the melting-point again taken. Softening took place at 48°, and an hour's heating at this temperature did not apparently change the condition of the substance. On heating to 50°, melting was fairly well completed. On allowing the same tube to stand over night, softening took place at a higher temperature, viz. 50.5°. There was still a small amount of the substance unmelted at 54.6°, and at 57° the crystals had entirely disappeared. The latter experiment lasted 105 minutes.

There was a marked difference between the recently melted hydrate and that which had stood for some time, in that the former substance was much more completely melted at 50° than the latter. That this was not due to the presence of a second form, but solely to dissociation products which had not combined, was shown by the following experiment.

Chloral hydrate was fused in a small test-tube and cooled as quickly as possible with water. The melt was well stirred, and as soon as the mass had assumed the solid state, the tube was broken, the contents taken out and well pressed between folds of filter-paper. A certain amount of oily substance was absorbed by the paper. When the crystals were dry they were transferred to a melting-point tube, sealed in, and compared with the fresh crystals, both tubes being attached to the same thermometer.

Both the tubes behaved in an identical manner. The melting-point was 50.4°–50.6°.[1]

In the course of an investigation of polymorphous substances, Pope had examined chloral hydrate crystallographically and has stated that the crystals formed on the solidification of chloral hydrate are different in form from those of the ordinary chloral hydrate, or to those which crystallize from chloroform. I have repeated Pope's work in this direction, in which I had the assistance of Prof. Gill, to whom I should like to acknowledge the very material help he has given me. According to Pope, on cooling chloral hydrate under a microscopic cover slip, long needles appear which are uniaxial and thus differ essentially from those deposited from chloroform, which are monosymmetric, and therefore cannot possess this optical property. Moreover the uniaxial crystals in the course of some days change to monosymmetric plates identical with the unfused substance. I have repeated Pope's work in this direction and have been able to follow the change which takes place, but not to the extent which Pope has shown in his paper. Furthermore, it is quite possible that the acicular crystals which appear on standing are not in reality uniaxial, but have so small an optical angle that they appear to possess this quality except when examined with the utmost care. Or what is also not at all unlikely, the large needles consist of aggregates of monosymmetric plates which behave very similarly to a uniaxial crystal. The breaking down of these segregates does occur as Pope has shown in his photomicrographic plates. That these acicular crystals do not differ in their behavior from ordinary chloral hydrate was shown

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[1] In a recent paper (Chem. News, 80, 270 (1899)) Kuhara and Chikashigé have proposed the determination of melting-points by heating the substance between microscopic cover glasses, and have found the melting-point of chloral hydrate identical with that of Meyer and Dulk (Liebig's Annalen, 171, 75 (1874)). The latter observers probably gave the point at which the last traces of crystals disappeared in the capillary tube. In the method of Kuhara and Chikashigé it is possible that the high melting-point is due to the small amount of the vapor phase allowed by the closely approximating surfaces of the glass plates. Hence, dissociation would have a relatively small effect on the melting-point, and the specimen could be heated to a high temperature without fusing the substance.

by the following experiment. Fresh crystals were melted in a small beaker immersed in a water-bath and held above the melting-point sufficiently long to permit of any change which could take place. The melt was cooled and on the appearance of crystals the liquid was removed by a small inverted funnel tube, the mouth of which was covered with cambric. As soon as the liquid was removed by exhaustion, the remaining crystals were taken out, dried with filter paper, and compared at once with the original substance. No difference between the two tubes could be observed.

The crystallographic examination shows that the form appearing on first cooling the melt consists exclusively of the acicular crystals described by Pope.

As a footnote to Pope's paper appears the suggestion made by Armstrong that the two forms may be represented by different structural formulæ, one being a hydrate of chloral

$$CCl_3COH.H_2O.$$

The other corresponding to a dihydric alcohol,

$$CCl_3.CH(OH_2).$$

Were these two structurally different compounds present in the melt, one would expect that on cooling to the solidification point the solution being saturated with respect to one form only, but one of the crystals would grow. That this is not the case is shown by the behavior of the melt. On cooling the fused chloral hydrate quickly to 46° and inoculating the supercooled mass with the two forms of crystals, solidification takes place equally rapidly. No trace of the temporary disappearance of either of the two forms can be observed. This is analogous to the classic example of sulfur. When this element is melted in a U tube and the melt in each of the arms sown with crystals of rhombic and monoclinic sulphur respectively, both forms of crystals grow, showing the production at the same temperature of both forms from one modification in the melt. The two crystalline forms also behave similarly when heated in vacuo. This was shown by a repetition of the Ramsay and Young experiment.

The thermometer was coated with chloral hydrate and allowed to stand three weeks. The coating which in this instance may be assumed to have changed to the truly monosymmetric crystals behaved on heating at 22 mm exactly as did those which were allowed to stand but a few hours.

To determine the equilibrium point, sealed tubes containing fused chloral hydrate and also the fresh crystals were brought into a bath regulated carefully by means of a calcium chlorid regulator, at 46.5° liquefied chloral hydrate solidifies while the crystals remain unchanged. At 48° the crystals melted after eighteen hours' heating and the mass after resolidifying melted again at 47.5°. It is thus safe to assume that the point for stable equilibrium for solid chloral hydrate with solution and vapor is between 46.5° and 47.5°.

To sum up the results of the work described in this paper, it may be said:

I. Chloral hydrate exists in but one modification in the melt.

II. The differences in the observed melting-point are due to dissociation phenomena and not to the presence of two forms in the melt.

III. The melting-point of undissociated chloral hydrate lies above 72°.

IV. The two forms described by Pope behave similarly on heating.

V. The sublimation pressure for undissociated chloral hydrate at 72° is about 22 mm.

VI. The stable triple point for chloral hydrate and the dissociation products is about 47°.

The experiments detailed in this paper were performed in the laboratory of Professor Bancroft.

Cornell University

THE RELATION OF THE TASTE OF ACID SALTS TO THEIR DEGREE OF DISSOCIATION

BY LOUIS KAHLENBERG

Investigations on the taste of dilute solutions of acids, when regarded in the light of the theory of electrolytic dissociation, have yielded the general result that sour taste is due to hydrogen ions and that its intensity varies as the concentration of the hydrogen ions in the solution. According to Richards,[1] sulphuric, nitric, hydrobromic, and hydrochloric acids can still be detected by the sense of taste in solutions somewhat less than *n*/1000. My own tests place the limit at *n*/800, at which dilution the taste is only astringent, while at *n*/400 it is slightly sour. It will be seen from this that the sense of taste is indeed a fairly delicate means of detecting acidity. Richards observed that while the sour taste of tartaric, citric, and acetic acids diminishes in the order named and hence agrees qualitatively with the dissociation theory, the quantitative agreement is not satisfactory, acetic acid, for instance, having a sour taste at least as strong as hydrochloric acid of one-third the equivalent concentration, whereas the former acid is dissociated to only about one-fourteenth the extent of the latter. The results of my tests[2] with acetic acid are similar to those of Richards, for I found that acetic acid has about four times as sour a taste as one would expect according to the dissociation theory.

The object of this article is to investigate the taste of the acid sodium salts of a number of dibasic organic acids, and also of the acid salts of citric acid, and to view the results in the light of the theory of electrolytic dissociation.

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[1] T. W. Richards. Amer. Chem. Jour. 20, 121.

[2] L. Kahlenberg. Bull. Univ. of Wis. 2, 1-31. Ref. Jour. Phys. Chem. 3, 66 (1899); Zeit. phys. Chem. 29, 343 (1899).

The acid sodium salts of the following acids were tested: oxalic, malonic, succinic, malic, tartaric, fumaric, maleic, and citric. The method of investigation was as follows: Solutions containing one gram-molecule of the acid salts in 100 liters were prepared; these were diluted successively with equal volumes of water. All of the solutions were tasted by myself by holding 6 to 8 cc in the mouth for a few moments after it had been well rinsed with distilled water. Of course the results can not claim to be as free from bias as those that were obtained in my former investigations where a number of persons, who were entirely ignorant of the nature of the substances they were tasting, tasted the solutions. My previous work, however, has taught me that my own sense of taste is what one would call normal; and the data given below I deem perfectly reliable, as I did not work with solutions so dilute that their taste was not clearly defined. The taste of solutions of the acid sodium salts of malic and tartaric acids was compared with that of a very dilute solution of hydrochloric acid of known strength. In these tests the method of experimentation employed in my previous investigations[1] was strictly followed, five persons serving as subjects. The results of these tests are also given below.

The degree of the hydrogen dissociation of acid sodium salts has been determined by means of the method of sugar inversion by J. E. Trevor[2] and also more recently by W. A. Smith.[3] The figures found are, as is well known, surprisingly low. The following table gives the percentage of hydrogen dissociation in the case of the acid sodium salts in question and also the volume in liters in which one gram of hydrogen ions is contained. With the exception of the figure for oxalic acid, the results are those of Smith. With but few exceptions the results of Trevor and those of Smith agree tolerably well. For the present purpose it is immaterial whether the results of the one or those of the other be used, as the general conclusion would remain the same.

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[1] l. c.

[2] Zeit. phys. Chem. 10, 321 (1892).

[3] Ibid. 25, 217 (1898).

Acid sodium salt of	H dissociation in percent when 1 g-mol is present in 128 liters	1 gram H ions is contained in
Oxalic acid	4.37	2929 liters
Malonic "	0.50	25600 "
Succinic "	0.159	80500 "
Malic "	0.719	17800 "
Tartaric "	2.800	4571 "
Fumaric "	1.52	8421 "
Maleic "	0.55	23273 "
Citric "	....	....
Mono Na salt	1.92	6666 "
Di Na salt	0.060	213333 "

Assuming that sour taste is due to hydrogen ions, it follows from these results (and the fact above mentioned, that the sense of taste is able to detect the presence of the strong mineral acids at no greater dilution than one gram-molecule in 1000 liters) that none of the salts given in the table ought to have any sour taste at all when one gram-molecule is contained in 128 liters. Now as a matter of fact they all have a sour taste at this dilution, and some of them even at much higher dilutions as the following data show.

Acid sodium oxalate is very plainly sour at the concentration 1 g-mol in 200 liters, and even at 1 g-mol in 400 liters it is still distinctly though of course faintly sour.

Acid sodium malonate is distinctly, though slightly, sour at 1 g-mol in 200 liters; while at 1 g-mol in 400 liters it is slightly astringent.

A solution of acid sodium succinate containing 1 g-mol in 200 liters is still distinctly sour, but it also has the disagreeable taste characteristic of the free acid.

Acid sodium malate is distinctly sour at 1 g-mol in 200 liters, but slightly astringent at 1 g-mol in 400 liters.

A sodium bitartrate solution containing 1 g-mol in 200 liters is very distinctly sour; while at 1 g-mol in 400 liters it is astringent or very slightly sour.

Acid sodium fumarate is distinctly sour at 1 g-mol in 100 liters, and still plainly, though faintly, sour at one-half this strength. A 1 g-mol in 400 liters it is slightly astringent.

The acid sodium salt of maleic acid tastes sour at 1 g-mol in 100 liters, and it has in addition the disagreeable taste characteristic of maleic acid. At 1 g-mol in 200 liters the acid salt has a slightly astringent effect.

Mono-sodium citrate is very plainly sour at 1 g-mol in 200 liters; while at 1 g-mol in 400 liters it is weakly but still distinctly sour. At one-half the latter strength the solution is very faintly sour or astringent.

Di-sodium citrate is slightly sour at 1 g-mol in 100 liters, while at one-half this concentration it is very faintly sour or simply astringent.

In addition to this, I found by direct tests[1] on five persons that a solution of acid sodium malate of 1 g-mol in 50 liters is about as sour as a solution of hydrochloric acid containing 1 g-mol in 140 liters; again, a solution of acid sodium malate of 1 g-mol in 100 liters is about as sour as a solution of hydrochloric acid of 1 g-mol in 320 liters. A solution of sodium bitartrate containing 1 g-mol in 100 liters is as sour as a solution of hydrochloric acid containing 1 g-mol in from 280 to 300 liters. A difference in the quality of the tastes of these dilute solutions of hydrochloric acid and the sodium bimalate and sodium bitartrate respectively could not be detected by the persons tested or by myself.

It is clear from the facts presented that the sour taste of solutions of these acid sodium salts can not be ascribed to the hydrogen ions present for there are too few of them. The question then arises,—to what is the sour taste of these solutions due? Looking at the matter from the standpoint of the theory of electrolytic dissociation, the undissociated molecules and also the bivalent anions in the solutions in question are relatively very few in number, while sodium ions and monovalent anions of the general formula $\overset{-}{H}Ac$ are abundant. Now as sour taste is not produced by sodium ions,[2] it follows that it must be ascribed

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[1] These experiments were conducted in the same way that my previous tests on taste were made (l. c.) so that a detailed description is hardly necessary in this connection.

[2] For solutions of the normal sodium salts have no sour taste.

to the monovalent anions. We are led to the conclusion, then, that these particular anions produce upon the sense of taste an effect that is identical with that produced by hydrogen ions. It should be borne in mind in this connection that these anions are large complexes varying in chemical composition in the case of different salts, that they bear electrical charges opposite to those on hydrogen ions, and that they are much less mobile than the latter. It is therefore evident that the explanation of the sour taste of the solutions of these acid salts from the standpoint of the theory of electrolytic dissociation is unsatisfactory to say the least.

Laboratory of Physical Chemistry, University of Wisconsin,
Madison, December 1, 1899

THE ELECTROCHEMICAL EQUIVALENT OF CARBON

BY H. C. PEASE

Coehn[1] has determined the electrochemical equivalent of carbon when anode in concentrated sulfuric acid, and has found that carbon is tetravalent under these circumstances, the weight of a gram equivalent being three grams. There are no satisfactory data as to the weight of a gram equivalent of carbon when this substance is anode in fused potassium hydroxid, and the investigation of this point was, therefore, undertaken at the suggestion of Professor Bancroft.

It is not possible to make the determinations merely by weighing the carbon anode before and after the run, because the electrode takes up a very considerable quantity of the electrolyte. At first it was hoped that the amount thus absorbed might be estimated with some approach to accuracy by determining the gain in weight of a carbon cathode during the run; but this proved impracticable, owing to the rapid disintegration of the cathode. The experiments were, therefore, made with a carbon anode and an iron electrode; in other words, with the Jacques cell.

At the end of the run, the carbon was washed in boiling water until the latter gave no test for alkali. It was then submitted to a temperature of about 225° C. until all the moisture was driven off. There were two sources of error here. Firstly, the caustic potash might not be entirely washed out, and yet the water give no test for alkali. Secondly, the water might not be entirely driven off. On account of the hardness of the carbon, it was not found practicable to reduce it to powder before washing. The two operations of washing and of subsequent drying

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[1] Zeit. Elektrochemie, 3, 424 (1897).

were therefore carried on much longer than was apparently necessary. Two checks were also used to make certain that the caustic potash had been removed entirely. The carbons were washed and dried several times until their weight was constant to within five milligrams. After the final weighing the carbon was ground up, the powder washed and the wash-water evaporated to dryness. If the caustic potash had been completely removed, no solid residue would remain. In no case was any trace of potassium hydroxid or potassium carbonate found. One of the carbons was washed in cold instead of hot water, and it was found that even in this way all the caustic potash could be removed.

Five experiments were made, the quantity of electricity being kept as near constant as might be, while the current and time varied. This was done to detect any change due to the variation in the strength of the current. The time varied from one and a half to five hours, and the current from one ampere to over three. The results are given in Table I.

TABLE I

Time in hours	1.5	2.0	3.00	4.0	5.0
Ampere hours	4.75	4.72	4.80	4.60	5.0
Average current	3.17	2.36	1.60	1.15	1.0
Carbon in grams	0.560	0.640	0.609	0.554	0.586
Equivalent weight	3.15	3.66	3.40	3.23	3.14

The values for the equivalent weight are calculated on the basis of 26.8 ampere hours per equivalent. Considering the possibility of error, the variation in the results, though large, is not excessive. The values for the equivalent weight of carbon vary between 3.14 and 3.66 as extreme limits, the average being 3.32. There is little doubt therefore but that the true value in caustic potash is 3.0, which is the value found by Coehn for carbon in sulfuric acid. That the values run uniformly high is probably due to a slight loss at the anode, due to disintegration, possibly also to a slight action of the caustic potash on the carbon, independent of the current. The second factor is probably not very important or there would be an apparent variation with the time. The first factor undoubtedly plays a part. Coehn obtained 3.5 for carbon in sulfuric acid when he disregarded it, and a mean value of about 2.9 when he took it into account. When working with fused caustic potash, as an electrolyte, it would be very difficult to make this correction, and I have not tried to apply it. The fact, however, that the variations are not functions of current or times, makes it probable that they are due to some such casual and arbitrary cause as disintegration.

This work was carried out in the physical chemistry laboratory of Cornell University, under the direction of Professor Bancroft.

Cornell University, June, 1897

NEW BOOKS

Introduction to Physical Chemistry. *By James Walker. 15 × 22 cm; x + 332 pp. New York: The Macmillan Company, 1899. Price: cloth, $2.50.* — In the preface the author says: "I have found, in the course of ten years' experience in teaching the subject, that the average student derives little real benefit from reading the larger works which have hitherto been at his disposal, owing chiefly to his inability to effect a connection between the ordinary chemical knowledge he possesses and the new material placed before him. He keeps his every-day and his physical chemistry strictly apart, with the result that instead of obtaining any help from the new discipline in the comprehension of his systematic or practical work, he merely finds himself cumbered with an additional burthen on the memory, which is to all intents and purposes utterly useless." This is painfully true. The real remedy for it has been pointed out by Ostwald and is to have the lectures on organic and inorganic chemistry delivered from a physical chemistry point of view. This will not happen to any great extent until no man can be appointed to a chair of organic or inorganic chemistry unless he has a working knowledge of physical chemistry. While we are nearing that ideal, it will be a long time before we reach it. In the meanwhile, we must do what we can.

This volume by Mr. Walker might well be made the basis of a course of lectures, intended to give students who do not mean to specialize in physical chemistry a general idea of the subject, while the same course might be taken with profit as an introductory one by those who expect to go farther in the subject. The author has been very successful along the lines that he has laid down, and his book can be recommended heartily. *Wilder D. Bancroft*

A Textbook of Physical Chemistry. *By R. A. Lehfeldt. 13 × 19 cm; xii + 305 pp. London: Edward Arnold, 1899. Price: cloth, 7/6.* — This is a very different book from the preceding one. It attempts to give more of the subject in fewer and smaller pages. The order followed is: determination of molecular weight; physical constants in relation to chemical constitution; the principles of thermodynamics; chemical dynamics of homogeneous systems; application of thermodynamics in chemical equilibrium; electrochemistry.

It is characteristic of this book that the chapter on molecular weights should be the first as well as the longest in the book. It seems to be the opinion of a great many people, including a number of physical chemists, that the chief end and object of physical chemistry and physical chemistry methods is to enable us to determine molecular weights. There are just two reasons for determining molecular weights: to get data which we can use in our quantitative studies, and to get data which the organic and inorganic chemist can use in preparing structure-formulas. Neither of these reasons is sufficient to justify the stress usually laid on determinations of molecular weights. As far as our quantitative studies go, we usually deduce the values needed from the experiments themselves and use the molecular weight determinations as a check. The organic chemist merely takes such data as suit his fancy, ignoring the remainder. This is not an exaggeration as the following two instances will show. At ordinary temperatures the vapor-density of acetic acid points to marked polymerization; but no organic chemist ever writes a structure-formula to indicate this. Alcohol in benzene gives thoroughly abnormal values, but no one attempts to do anything with these values. All that the organic chemist asks is that some value shall be found somehow which shall coincide with the formula as he wishes to write it.

To come back to the book, it is really surprising to see how much the author has succeeded in compressing into a small compass. He points out the actual error introduced by writing $(p - p')\,p$ instead of log p/p'; and calls attention to the fact that the molecular weight of the solvent as vapor appears in the van 't Hoff-Raoult formula. Reference is made to the 'convergence temperature' in the discussion of freezing-points; there is a most instructive pressure-temperature diagram with reference to the critical point; a brief account of the corresponding temperatures; and so on through every chapter. Of course, there are some unfortunate statements, such as the following on page 38: "If from a solution some of the solvent be frozen out, since the volume is diminished, the osmotic pressure of the remaining solution is increased; thus the osmotic pressure tends to resist the freezing, and the freezing temperature will be lower than that of the pure solvent." Such slips as this are infrequent and the reviewer is able to congratulate the author most heartily on everything except on the perverse order adopted. *Wilder D. Bancroft*

Kanon der Physik. *Die Begriffe, Principien, Sätze, Formeln, Dimensionformeln, und Konstanten der Physik. By Felix Auerbach. 16 × 24cm; pp. 12 + 522. Leipzig: Veit und Comp., 1899. Price: paper, 11 marks.*—On a previous occasion, the professor of physics at Jena gave us an excellent monograph on hydrodynamics. With the present work he adds a similarly useful volume covering the whole range of physics and addressed both to the special and to the general reader. It is the object of the book, to give clear-cut and intelligible statements of the concepts, principles, laws, equations, and constants, of physics in such a way as to represent the present stage of advancement of the subject. Written by a man of broad culture, there is much in the book which goes beyond the mere vernacular of physics, but it has been the author's chief aim to produce an encyclopedia in which the topics treated appear in orderly development. In this endeavor he has been successful. Anybody engaged in teaching physical science will find the book invaluable as an aid to the judicious selection of subjects for lecture purposes, to the same degree in which the book is itself a tribute to the balanced attainments of the German professor. As the "Kanon" is also to be of service to the reader not versed in the higher mathematics, there is necessarily much halting between self-evident and abstruse propositions, and the contrast is often amusing.

The book begins with an exposition of the foundations of dynamics, and continues with molecular physics (Chaps. I.–V.). The chapter on potential which follows is quite modern, including full consideration of hydrodynamic, elastic, and (further along in the book) thermodynamic potentials. Here, as elsewhere, the total absence of figures interferes with easy reading. The remainder, and nearly two-thirds of the book, is devoted to energy (Chap. VII.) and entropy (Chap. VIII.). In this respect, the division is to the reviewer's knowledge novel, and it may be questioned whether such a division is advisable, seeing that to consult the book one must look in two places instead of one. In the first of these chapters, the transformations of energy are considered with reference to numerical values only; in the other, with reference to the conditions of occurrence of the transformation. Hence the use of the term entropy is generalized to mean the quantity factor of any form of energy, and implying the existence of a correlative intensity factor which may be velocity, temperature, potential, etc. The two factors vary reciprocally, and all natural processes are characterized by a decrease of the availability factor and a corresponding increase of entropy. Apart from the introductory matter, the whole of physics is then divided between the two chapters in question. The information is throughout very full, the data well selected, the treatment modern, and the statements accurate and frequently suggestive. Thus, for instance, under dynamics, the principles of Maupertuis, Hamilton, D'Alembert, Gauss, Helmholtz, Hertz, and the equations of Lagrange, are treated in succession; under thermodynamics, much attention is given to the thermodynamic potential, and to the recent contributions of physical chemists. Maxwell's theory and the electromagnetic theory of light are presented in the symmetrical form due to Hertz and Heaviside. The paragraph on geometric optics gives a terse account of the valuable methods due to Abbe, etc. One leaves the book with a feeling of satisfaction over the uniformity of nomenclature which now prevails in all countries, thanks to the timely discoveries of Hertz; and it is interesting to contrast Auerbach's paragraph on magnetism with what would have been written in Germany ten years ago.

Carl Barus

Determination of Radicles in Carbon Compounds. *By Dr. H. Meyer. Translated by J. Bishop Tingle. 12 × 19 cm; pp. ix + 133. New York: John Wiley and Sons, 1899. Price: cloth, $1.00*—In this small book has been collected a very useful selection of reactions both qualitative and quantitative, which are used by the organic chemist in solving questions of constitution in the compounds of carbon. For the most part, the reactions are quantitative in character, and embrace the quantitative determinations of hydroxyl, methoxyl, carboxyl, amine, and diazo groups. A praiseworthy feature is the large number of references to original papers which are given under the various heads.

C. G. L. Wolf

Indicators and Test-papers. *Their source, preparation, application, and tests for sensitiveness. By Alfred I. Cohen. 13 × 19 cm; pp. ix + 249. New York: John Wiley and Sons, 1899. Price: cloth, $2.00.*—The author gives the methods of preparation, properties, and application of over seventy indicators, together with the methods of preparation and the rules for applying about the same number of test-papers. The book should prove very useful for reference.

Wilder D. Bancroft

Handbook of Practical Hygiene. *By D. H. Bergey. 14 × 20 cm; pp. 164. Easton, Pa.: The Chemical Publishing Co., 1899. Price: cloth, $1.50.*—This book, which is intended for students, is remarkable when looked on from a hygienic standpoint in that in treating the analysis of water and air, absolutely no reference is made to the importance of bacteriological examination. That a chemical examination of water can give but the faintest evidence of its suitability for sanitary purposes is admitted by all practical sanitarians. Without a biological analysis it is useless, and the two combined are also of small value unless combined with a careful investigation of the history and source of the water. Had some of the numerous methods for the determination of nitrates been replaced by a fuller summary of the interpretation of the results, in connection with the biological examination, the chapter on the analysis of water would assuredly have been more useful to the student. The book is by no means well balanced. *C. G. L. Wolf*

The Chemistry of Soils and Fertilizers. *By Harry Snyder. 13 × 17 cm; pp. ix + 277. Easton, Pa.: The Chemical Publishing Co., 1899. Price: cloth, $1.50.*—Professor Snyder has treated the chemistry of soils and fertilizers in such a way as to produce a book which may be read with profit not only by the student of agriculture, for whom it is primarily designed, but also by the practical agriculturalist, who too often employs haphazard measures at times when a little more care would give much more satisfactory results. The relation between crop production and soil exhaustion is clearly made out, as is also the proper treatment of farm manures in order to realize their maximum efficiency. A bibliography is appended. *C. G. L. Wolf*

Jacobus Henricus van 't Hoff. *By Ernst Cohen. 16 × 24 cm; 56 pp. Leipzig: W. Engelmann, 1899. Price: 1.60 marks.*—This is a brief sketch of van 't Hoff by one of his most promising pupils. From it we learn that van 't Hoff was born in Rotterdam, August 30, 1852. In 1869 he went to the technical school at Delft, where he stayed two years. In 1871 he went to the University at Leiden, special permission being necessary for this because he had never studied Latin. The first examination was passed in 1872, and then van 't Hoff went to Bonn to study under Kékulé. At the end of the year he returned to Holland, and, after a short stay in Paris under Würtz, took his doctor's degree in Utrecht on December 22, 1874. The twenty-fifth anniversary of this event has just been celebrated in Rotterdam, on which occasion his former pupils, following the good German custom, presenting him with a volume of their own work, a jubilee volume of the *Zeitschrift für physikalische Chemie*. The further details of van 't Hoff's scientific life are familiar to every chemist, with the possible exception of the fact that he had to wait two years after taking his doctor's degree before he could get an appointment.

To those of us who have had the pleasure of working in van 't Hoff's laboratory, of knowing the man himself, and of feeling the charm and enthusiasm of his manner, it is, even more than to others, an intense satisfaction to feel that we have every reason to look forward to at least another twenty-five years of research work, carried on under ideal conditions. *Wilder D. Bancroft*

REVIEWS

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

General

The genesis of Dalton's atomic theory. *H. Debus. Zeit. phys. Chem.* 29, *266* (*1899*). — Roscoe and Harden, in their book: "A New View of the Origin of Dalton's Atomic Theory," endeavored to prove that Dalton was led to the atomic hypothesis by considering the phenomenon of the diffusion of gases, and not by the empirical law of multiple proportion, as was formerly supposed. Debus combats this idea in the present (his third) paper, and brings forward a certain amount of interesting evidence from Dalton's notebooks. He further sharply criticizes several passages in Kahlbaum's translation of Roscoe and Harden's book. *A. P. S.*

Reply to H. Debus. *G. W. A. Kahlbaum. Zeit. phys. Chem.* 29, *700* (*1899*). — Kahlbaum defends himself against the charges of mistranslation preferred by Debus (preceding review) and quotes passages where the renderings of Debus himself are not above reproach. *A. P. S.*

Determination of the heat of combustion of some organic compounds. *P. Zoubow. Jour. Russ. Soc.* 30, *926* (*1898*). — The heats of combustion of certain liquid hydrocarbons, alcohols, ketones, and ethers of the aliphatic series were determined by Berthelot's calorimetric bomb. *C. E. L.*

One-Component Systems

Investigation of crystalline liquids, IV. *R. Schenck and F. Schneider. Zeit. phys. Chem.* 29, *546* (*1899*). — The beginning of this paper is devoted to a discussion of the vapor-tension curves for solid and liquid in the case of enantiotropic and monotropic substances. In the case of the former the vapor-tension curve for the liquid cuts the two curves for the solid forms above their point of intersection; here the form, stable at low temperatures, may have an instable melting-point, but goes over normally, on heating, without melting, into the other form, which has a stable melting-point. As an example, take rhombic and monoclinic sulfur. In the case of monotropic substances the vapor-tension curve for the liquid cuts the other two curves below their intersection; here one solid form is instable throughout its range and melts to an instable liquid, whereas the stable form has also a stable melting-point; this is illustrated in part at least by yellow and red phosphorus.

Finally, the vapor-tension curve for the liquid may meet the others at their intersection, in which case there is a quadruple point, the phases being vapor, liquid, and two solid forms.

The present paper brings forward a case where all of these possibilities are realized with one substance. Para-azoxyanisol melts at 116.8° to a crystalline liquid, and this in turn goes over at 134° to an isotropic liquid. The solid is stable below 116.8° and the crystalline liquid between 116.8° and 134°. By adding a second substance—benzophenone was the one used—the vapor-tension of the liquid can be so far reduced that its curve now cuts the curves for the solid and crystalline liquid below their intersection, and the substance becomes monotropic as experiment shows; for the solution on cooling goes over at about 113.5° (for a 5 percent solution), into the solid form; yet it is possible by cautious cooling to pass beyond this to 109°, where the crystalline liquid makes its appearance; it is instable, and on addition of a solid crystal goes over completely into that form with rise of temperature.

In view of the various ideas which are at present held regarding the nature of isomorphous mixtures (Cf. van 't Hoff, Zeit. phys. Chem. 5, 322; Bodländer. N. Jahrb. f. Min. Geol. u. Pal., Beilage 12) the author's experiments on liquid crystalline mixtures of *p*-azoxyanisol and *p*-azoxyphenetol are of interest. The solid modifications of these compounds are not isomorphous and the pure substances separate out on freezing. It is found that for dilute solutions the depression of the freezing-point is, with a fair degree of accuracy, proportional to the quantity of azoxyphenetol; i. e. that these substances obey the laws for dilute solutions. If we grant that the only difference between liquid and solid crystals is in the degree of viscosity, the same conclusion would apply by analogy to the latter. *A. P. S.*

On the change of volume accompanying the transformation of boracite. *W. Meyerhoffer. Zeit. phys. Chem.* 29, *661* (*1899*).—Boracite goes over at 260° from rhombic into regular crystals. The author studied this change with the micro-dilatometer, with which, in spite of the small quantity of substance available (0.8 g), satisfactory results were obtained. The liquid employed was mercury. Besides determining the temperature more definitely than had been done before, Meyerhoffer found that the change from the rhombic to the regular form was accompanied by a contraction; hence the point would be lowered by increasing the pressure. *A. P. S.*

On the enantiotropy of tin. *E. Cohen and C. Van Eyk. Proc. Roy. Acad. Amst.* 1899, *77*.—The authors consider the phenomenon, well known amongst the tin traders of Russia, that pure tin falls into a grey powder when exposed to great cold. They found from preliminary work that the change is caused by a transition of one variety into the other as

$$\text{Grey tin} \rightleftarrows \text{white tin.}$$

The salt, ammonium stannic chloride, was found to accelerate the change and to sharpen the transition point. For instance, the change of white tin into grey tin, which without the salt took 24 hours to change at −83°, took only 6 hours with a 10 percent solution of the salt. The phenomenon was found to be quite analogous to the transition of a hydrated salt. To measure the transition temperature two methods were used; the dilatometric and the electric. From the former the point was found to be between +10° and +20°. By the latter method in a transition cell of

White tin — 10% ammonium stannic chloride — grey tin,

which was set up, the change was found to occur at 20°. The authors conclude by saying: "Since all tin articles in every-day use consist of the white modification, the above research leads to the striking result that our whole tin-world exists, except on a few hot days, in the metastable condition." *H. T. B.*

The continuous transformation, solid-liquid. *G. A. Hulett. Zeit. phys. Chem.* 28, *629* (*1899*). —The author was unsuccessful in his attempt to find a critical point for solid and liquid. He has, however, measured the change of the melting-point with the pressure for a large number of substances. In nearly every case, the change of melting-point was proportional to the change of pressure, a result which does not agree with the data obtained by Tammann, and seems to exclude the possibility of the liquid from being stable at low temperatures. *W. D. B.*

On a modification of Van der Waals's equation of condition. *L. Boltzmann and H. Mache. Wied. Ann.* 68, *350* (*1899*). — From Boltzmann's "Vorlesungen über Gastheorie" the modification of Van der Waals's gas equation connecting p the pressure on unit surface, v the specific volume, and T the absolute temperature, is found to be

$$\left(pT+\frac{a}{v}\right)\left(v-\frac{1}{3}b\right)=rT\left(v+\frac{2}{3}b\right).$$

Taking the results of Amagat for CO_2, the authors compare the experimental with the results deduced from this formula. They find the agreement at low temperatures is not good. They therefore propose the form

$$\left(p+\frac{a}{v^2}\right)\left(v-b+\frac{C}{v^2+d}\right)=rT.$$

which gives a better agreement at the lower points, but yet diverges somewhat for the higher. *H. T. B.*

The specific gravity of liquid air and other liquefied gases. *A. Ladenburg und C. Krügel. Ber. chem. Ges. Berlin*, 32, *46* (*1899*). —The method used was the immersion of a glass rod whose specific gravity at 4° was known in the liquid investigated. A correction of 0.005 was added for the contraction of glass at the temperature of the gases.

The specific gravity, as was expected, rose in the case of air with increasing oxygen content. Fresh air had a specific gravity of 0.9951. This was found on analysis to contain 53.83 percent of oxygen. The authors calculate the specific gravity of air containing 20.9 pct and give it as 0.8707. Ethylene had a specific gravity of 0.6585 at —169° and of 0.5710 at — 105.4°. *C. G. L. W.*

Specific gravity of liquefied gases. *A. Ladenburg and C. Krügel. Ber. chem. Ges. Berlin,* 32, *1415* (*1899*). — The authors have examined the specific gravity of air, ethylene, and oxygen, both by the methods of immersion of silver and glass weights and with a pyknometer. The specific gravity of air is found to be three percent lower through the immersion of glass than by weighing a silver weight. They were unable to explain this difference through change in the coefficient of expansion of glass and silver at low temperatures. The results correspond with those of Dewar fairly closely. *C. G. L. W.*

The pentavalent nitrogen atom. *Edgar Wedekind. Ber. chem. Ges. Berlin,* 32, *511* (*1899*). — Wedekind has examined various compounds formed by the union of substituted amins with alkyl iodids. The isomers formed by the union of allyl ethyl anilin with benzyl iodid, ethyl benzyl anilin with allyl iodid, and benzyl allyl anilin with ethyl iodid, are advanced as cases of steroisomerism. *C. G. L. W.*

The pentavalent nitrogen atom. *Cases of inactive stereoisomerism. Edgar Wedekind. Ber. chem. Ges. Berlin,* 32, *517* (*1899*). — In this paper the author describes the preparation of a number of compounds analogous to those mentioned in the preceding review. *C. G. L. W.*

Note on perborates. *S. Tanatar. Zeit. phys. Chem.* 29, *162* (*1899*). — Ammonium and sodium perborates (3, 562) decompose slowly on standing, more rapidly in the presence of carbon dioxid, most rapidly in the presence of alkaline hypochlorites or of cobalt oxid. *W. D. B.*

Two-Component Systems

On the solidification of liquid mixtures of tautomeric substances. *H. W. Bakhuis Roozeboom. Zeit. phys. Chem.* 28, *289* (*1899*). — A discussion of the equilibrium phenomena when the change of one modification into the other is prevented or limited at certain temperatures by the existence of passive resistances. The most general case is the one in which neither substance changes at all at its melting-point into the other, the curves for one-sided equilibrium cutting the temperature axis above the melting-points. With a system of this sort, each modification will melt and freeze at the same temperature, provided it has not been heated too high above its melting-point. The author takes up in detail the behavior of the system when it has been heated to some temperature in the zone of one-sided equilibrium and when it has been heated to some temperature in the zone of reversible equilibrium. The case is then taken up in which the curves for one-sided equilibrium cut the fusion curves. This is an intermediate stage between the first case and the one for completely reversible equilibrium already worked out by the reviewer. It is a pleasure to record the fact that the equilibrium phenomena for systems without passive resistances had been worked out by the author long before the subject had been taken up at all by the reviewer. *W. D. B.*

Three cases of desmotropism. *P. Rabe. Ber. chem. Ges. Berlin,* 32, *84* (*1899*). — This is a preliminary paper on benzylidene acetoacetic ester, ethylidene acetoacetic ester, and a compound previously investigated by Goldschmidt and Kisser found by the condensation by hydrochloric acid of carbon with ethyl acetoacetate. From somewhat inconclusive data the author believes, in contradistinction to Schiff, that it is impossible by the chemical means which he used to isolate either of the enol or keto forms in substances consisting of these two modifications. He speaks of the method of using an excess of cold concentrated sulfuric acid as a refiner method, and as somewhat of a novelty, although this method of obtaining a pure aldol modification was used in the case of oxymethylene phenyl acetic ester over three years ago. *C. G. L. W.*

Solubility and melting-point as criteria for racemate compounds, pseudoracemic mix-crystals and inactive conglomerates. *H. W. Bakhuis Roozeboom. Zeit. phys. Chem.* **28**, *494* (*1899*). — From a solution of two optically active isomers, there may crystallize an inactive compound, a solid solution, or the two isomers. A mixture of two solids, such as occur at a eutectic point, is called a "conglomerate". This new term is a most excellent one and will undoubtedly come into general use. The author shows how one can distinguish between compounds, solid solutions, and conglomerates by a study of the solubility curves. If we have a conglomerate, addition of either of the isomers will leave the composition of the solution unchanged. If we have a compound, addition of either isomer will change the composition of the solution until the solution is saturated with respect to that isomer, the composition of the solid phase remaining unchanged until the saturation point is reached. If we have a solid solution, addition of either isomer will cause a continuous change in the composition, both of solution and of solid phase.

The author next discusses the freezing-point curves for systems in which conglomerates, mix-crystals, or racemate compounds can exist in equilibrium with solution and vapor, then taking up the intermediate cases in which a racemate is formed from a conglomerate, a conglomerate from a racemate, or a racemate from a solid solution at temperatures below those at which the solution is a stable form. If organic chemists would master the contents of this article, there would be no confusion henceforth as to the existence or non-existence of racemates. *W. D. B.*

The cryoscopic behavior of alcohols. *Wilhelm Biltz. Zeit. phys. Chem.* **29**, *249* (*1899*). — The molecular weights of thirty-one different alcohols were determined by the freezing-point method, using benzene as solvent. Naphthalene was also used as a solvent in the case of cetyl, heptyl, and octyl alcohols. Generally five or six determinations were made with each alcohol, the concentration of the solutions varying so as to give depressions ranging from about 0.1° to 0.2° for the most dilute solutions, to about 2° to 4° for the most concentrated ones. The percentage deviation of the found molecular weight from the calculated is determined in each case. The general result obtained is that with increasing concentration of the solutions, the primary alcohols show the greatest increase of molecular weight, the secondary alcohols show less increase, and the tertiary least, which is a confirmation of the author's previous work. The deviation from the normal molecular weight is very great; in the case of methyl, ethyl, and *n*-propyl alcohol, it amounts to from 200 to 250 percent in the strongest solutions tested. The higher the molecular weight of the alcohol, the less the deviation. Unsaturated alcohols show more deviation than corresponding saturated ones. The results of Ramsay and Shields and also those of Traube on association are mentioned in this connection by the author who does not attempt, however, to draw any further conclusions from them.

The work of the author is exhaustive as far as the solvent benzene is concerned. It shows conclusively that the lowering of the freezing-point is due not simply to the number of dissolved molecules, but also to their individual nature. The behavior of these alcohols in other solvents ought also to be studied thoroughly. The 'influence of the solvent' is of the highest importance. The idea of combination between solvent and solute is not considered by the author.

L. K.

The solubility of the halid salts of zinc and cadmium. *R. Dietz. Ber. chem. Ges. Berlin,* 32, *90 ; Zeit. anorg. Chem.* 20, *240* (*1899*). — The author has examined the solubility of the bromids, chlorids, and iodids of zinc at different temperatures. Anhydrous zinc chlorid is stable in equilibrium with solutions above 23°. Below this temperature it changes into hydrates containing 1.5, 2, 2.5 and 3 molecules of water, the inversion temperatures being 23°, 19°, 13°, and 7°. The monohydrate is instable at all temperatures, but the solubility curve has been determined.

It is possible to follow the solubility of the different hydrates below the inversion point without observing any marked change in the composition of the crystal precipitates. By the introduction of a crystal of a hydrate containing more water, the crystals change to the modification stable at that temperature. Solubility determinations were made with $ZnBr_2$, ZnI_2, $CdCl_2$, $CdBr_2$ and CdI_2.

C. G. L. W.

Solubility of metallic nitrates. *R. Funk. Ber. chem. Ges. Berlin,* 32, *96; Zeit. anorg. Chem.* 20, *393* (*1899*). — This paper is a continuation of the preceding ones. The salts examined were the nitrates of magnesium, zinc, manganese, iron, cobalt, nickel, copper, and cadmium. The solubilities of the nitrates of the salts at different temperatures are given. Magnesium nitrate forms two hydrates. The monohydrate is stable below −20°, changing at that temperature to the hexahydrate. Zinc nitrate forms in addition to the hexahydrate two others containing respectively three and nine molecules of water. Cobalt and nickel form similar compounds to zinc. Copper forms a hexa- and trihydrate ; cadmium nitrate crystallized as a tetra- and monohydrate. Funk states that the solubility of these salts increases inversely as the temperature of the cryohydric points. *C. G. L. W.*

Mutual solubility of liquids ; vapor-pressure and critical points of mixtures. *J. P. Kuenen and W. G. Robson. Phil. Mag.* [*5*] 48, *180 ; Zeit. phys. Chem.* 28, *342* (*1899*). — When a two-component system having two liquid layers and vapor is heated high enough, a critical temperature will be found. It has hitherto been assumed that the two liquid phases would become identical. The author shows that one liquid phase may become identical with the vapor phase. This occurs experimentally with ether and water at 201° ; for ethane with methyl alcohol at 31.6° ; with ethane and ethyl, propyl, isopropyl, and butyl alcohols at 40.7°, 41.7°, 44°, and 39.8° respectively. With these last four alcohols a lower critical temperature was observed at which the two liquid layers became identical. This temperature was 31.9°, 38.7°, 38.1° for ethyl, propyl, and butyl alcohol respectively. The lower critical temperature could not be determined accurately for ethane and isopropyl alcohol, owing to impurities in the latter. With ethane and methyl alcohol no lower critical temperature could be found even at – 78°. With ethane and isoamyl alcohol two liquid phases could not be obtained at any temperature. With ether and water the composition of the vapor lies between that of the two liquid phases, but this is not the case in the other systems. *W. D. B.*

Comment on the vapor-pressure of solutions with volatile components. *R. A. Lehfeldt. Phil. Mag.* [*5*] 48, *215*; *Zeit. phys. Chem.* 29, *498* (*1899*).— When a small amount of the volatile liquid A is dissolved in the volatile liquid B, the vapor-pressure relations are said to be expressed by the formula:

$$\frac{p}{\pi_B}=\frac{1-\zeta}{1-\eta},$$

where p is the total vapor-pressure of the solution, π_B the vapor-pressure of pure B, ζ is the ratio of the number of reacting weights of A to the number of reacting weights in the liquid, η the ratio of the partial pressure of A to the partial pressure of A to the partial pressure of B in the vapor. This formula is said to be a necessary consequence of the thermodynamics; but this seems doubtful because the formula is not right. For the case in which A is non-volatile, the formula reduced to $\frac{p-p'}{p}=\frac{\eta_A}{\eta_B}$, which is indeed the Raoult formula, but which is inaccurate, both theoretically and experimentally. The only other point of interest in the paper is that the experimental variations from the formula are greater when alcohol is one of the components than when it is not. Even this was known before.

At one time Mr. Lehfeldt was seized with the praiseworthy idea of studying concentrated solutions; but the meretricious temptations of the 'ideal' solution have been too much for him. There are so few people who are interested in exact theory that the defection of a promising recruit is a cause for deep regret. *W. D. B.*

The boiling-point of aqueous solutions of colloidal salts. *F. Krafft. Ber. chem. Ges. Berlin*, 32, *1584* (*1899*).—This paper is a continuation of the work on the author's 'Theory of colloidal solutions,' Ber. chem. Ges. Berlin, 29, 1334 (1896). It shows that the pure sodium salts of the higher aliphatic acids behave, according to circumstances, as colloids or crystalloids, and not only they, but many other salts occupy a place between these two classes.

In contradistinction to Kahlenberg and Schreiner (3, 416), he shows that aqueous solutions of potassium and sodium palmitate, oleate, and erucate, even when highly concentrated, have a boiling-point identical with that of pure water, but that the introduction of substances such as sodium chlorid raises the boiling-point of the soap solution to the height required by the weight of the salt introduced. In other words, the soap solution behaves toward the salt as does pure water.

In highly concentrated soap solutions the surface-tension is so great that a small elevation of temperature is found. The view of Kahlenberg and Schreiner of "pseudo-ebullition" is held to be unnecessary. In the case of soaps dissolved in absolute alcohol, a close approximation to the normal monomolecular rise was found proving that in this medium the salt is not split up. Methods are given for the preparation of pure soaps. *C. G. L. W.*

The condition of crystallization of colloid salt solutions. *F. Krafft. Ber. chem. Ges. Berlin*, **32**, *1596* (*1899*). — Krafft has propounded the two theories, first that colloid fluids or solutions contain the fluid substance in the molecular condition, and second, that colloidal fluid molecules rotate in extremely small paths or planes. Hence one may assume a definite structure for solutions of this kind. When a colloid fluid crystallizes one deals with a simple cessation or change in the character of the oscillation or a change in the reciprocal position of the molecule, whereas in gelatinization or in the solidification of an amorphous substance, the motion is greatly slowed down, but the spatial relations remain as in the fluid condition. *C. G. L. W.*

Compounds of Li, Na, and K, with Hg determined from their specific volume. *E. Maey. Zeit. phys. Chem.* **29**, *119* (*1899*). — From the contraction in volume that occurs when these three alkali metals react with mercury, the author concluded that the following compounds exist: — $NaHg_5$, $NaHg_2$, $NaHg_1$, Na_3Hg; — KHg_{11}, KHg_5, KHg_3, KHg_2, KHg, — $LiHg_5$, $LiHg_3$, $LiHg_1$, Li_3Hg. *L. K.*

A method of determining the specific heat of solutions. *D. Konowalow. Jour. Russ. Soc.* 30, *353* (*1898*). — The principle of the method is that of the well-known method of Thomsen, the essential modification being the employment as source of heat of a simple device for mixing definite quantities of concentrated sulfuric acid and water instead of the Thomsen hydrogen burner. *C. E. L.*

On the determination of the specific heats of salt solutions by the method of D. Konowalow. *E. Biron. Jour. Russ. Soc.* 30, *355* (*1898*). — A description of the apparatus, its manipulation, calculation of results, and discussion of their errors, together with data for a number of solutions of the commoner salts. The method seems to be both accurate and rapid. *C. E. L.*

Remarks on the chemical theory of solutions. *A. A. Jakowkin. Jour. Russ. Soc.* 30, *28* (*1898*). — The author thinking that certain views of his on the theory of solutions were not treated in the right way by G. Tanatar (Classification of Substances by Means of their Solubility, Moscow, 1895) criticizes some points in the treatment. Nothing of general interest, however, is brought out. *C. E. L.*

Poly-Component Systems

On reciprocal salt pairs, II. *W. Meyerhoffer and A. P. Saunders. Zeit. phys. Chem.* **28**, *453* (*1899*). — A study of the system made up of these constituents, Na_2SO_4, KCl, NaCl, K_2SO_4, and H_2O, together with a theoretical discussion of the general case. The following inversion temperatures were determined.

With sodium sulfate and water, the decahydrate and the anhydrous salt are in equilibrium with solution and vapor at 32.35°. With sodium chlorid and water, $NaCl2H_2O$ and NaCl are solid phases at 0.15°. The addition of potassium chlorid in excess lowers this point to — 2.35° while the addition of hydrated sodium sulfate lowers it to — 2.85°. Hydrated sodium sulfate, anhydrous sodium sulfate, and sodium chlorid are solid phases at 17.9°, when there is no potassium salt in the solution; $Na_2SO_410H_2O$, Na_2SO_4, and $K_3Na(SO_4)_2$ at 30.1° when there is no chlorid in solution. At 44° there is a sextuple point with $Na_2SO_410H_2O$, Na_2SO_4, KCl, and NaCl as solid phases. *W. D. B.*

On the equilibrium relations of carnallite. *J. H. van 't Hoff and W. Meyerhoffer. Zeit. phys. Chem.* 30, *64* (*1899*). — Reviewed (3, 508) from Sitzungsber. Akad. Wiss. Berlin, 1897, 487.

Equilibria in the system: Water, phenol, and anilin. *F. A. H. Schreinemakers. Zeit. phys. Chem.* 29, *577* (*1899*). — The present investigation is, in a sense, a sequel to the one on water, alcohol, and succinonitrile (Zeit. phys. Chem. 27, 95). In that case the equilibria were represented, using the triangular method, by two binodal curves which would coalesce to one at low temperatures if the system remained stable; the present case is an example in which only one binodal curve exists even at ordinary temperatures.

The first part of the paper is devoted to a more complete study than had previously been made of the equilibria in the three binary systems: water-phenol, water-anilin, phenol-anilin. The results are in the first two cases systems composed of melting-point curves and the familiar solubility curves first mapped out by Alexéjeff. The third system is composed of the melting-point curves of (1) phenol, (2) the compound $C_6H_5NH_2HOC_6H_5$, (3) anilin.

The method used in studying the three-component system was to make series of determinations, each series being made with a fixed amount of two components and a varying amount of the third. These mixtures were sealed up and their clouding temperatures determined. For a given mixture of phenol and anilin the clouding temperature rises at first with increasing additions of water, reaches a maximum and then falls. This maximum is called by Schreinemakers the critical mixing temperature, and he distinguishes this point from that of critical solution, the latter being the point at which the two layers attain the same composition. The points are identical where only two components are present. The author discusses at some length the two- and three-dimensional figures obtained from his results, but leaves most of the theoretical considerations to a later paper.

The conclusion is devoted to a brief discussion of the systems: water, anilin, and sodium chlorid, and water, phenol, and sodium chlorid. It is found that addition of salt or anilin raises the critical mixing temperature of water and phenol, whereas addition of phenol lowers that of water and anilin. *A. P. S.*

The effect of binary electrolytes on the solubility of ternary electrolytes, the two electrolytes having no ion in common. *A. A. Noyes and E. S. Chapin. Zeit. phys. Chem.* 28, *518* (*1899*). — Addition of ammonium chlorid to a solution saturated with respect to calcium hydroxid causes more of the latter to go into solution. The authors develop the theory for this case along orthodox lines, and test it experimentally. The result is surprisingly good, though one might wish that the authors had called attention to the fact that the difference between the calculated and the found values has the same sign in all three measurements, and that the percentage variation increases with increasing concentration of ammonium chlorid. There is every reason to suppose that the discrepancy is real and is not due to experimental error. *W. D. B.*

On the diminution of solubility. *S. Tolloczko. Jour. Russ. Soc.* 30, *794* (*1898*). — The author gives a method of measuring the diminution of solubility of one liquid in another, caused by the addition of a substance soluble in but one of the liquids, and applies it with the aid of Nernst's law of diminution of solubility to the determination of molecular masses. The apparatus consists of a small flask with slender graduated neck and glass stopper. This is filled with ether and water, in such proportions that the meniscus separating them is near the end of the scale. The substance under examination is then added, and the shifting of the meniscus, after equilibrium is re-established, is taken as a measure of the change in solubility.

Nine organic compounds were investigated with quite satisfactory results, even in concentrated solution, and it was found that the ether exerted no associative or dissociative action.

Some determinations of the solubility of ether in water at ordinary temperatures are also given, and it is shown how the apparatus may be employed in the finding of the specific gravity of liquids. *C. E. L.*

The transition temperature of neutral strychinine tartrate. *A. Ladenburg and G. Doctor. Ber. chem. Ges. Berlin*, 32, *50* (*1899*). — This article is a continuation of the work on partial racemization. The specific gravity of the anhydrous neutral racemate of strychinine was found to be $\frac{20}{4}$, 1.36653, while those of the *d* and *l* tartrate were 1.3405 and 1.43218 respectively. The rotation for these salts is given $[\alpha]_D \frac{20}{4}$.

$$-31.87924 + 3.7487\,p\,;\ -20.60725 + 0.9367\,p\,;\ -31.36342 + 1.3563\,p\,;$$

p denoting the percentage of the anhydrous salt in the solution. They find that the specific rotation increases with dilution. This is especially so with the racemate. They show that a mixture of racemic acid and strychinine yields a partially racemized compound. *C. G. L. W.*

Osmotic Pressure and Diffusion

On the nature of osmotic pressure. *F. Barmwater. Zeit. phys. Chem.* 28, *115* (*1899*). — The author looks upon osmotic pressure very properly as a measure of the affinity between solvent and solute. Starting from a kinetic standpoint, he deduces an unwieldy formula which he applies to Abegg's measurements. For electrolytic dissociation, he deduces the formula $k\sqrt[3]{x/v} = 1 - x$, and applies it in the case of strong electrolytes. He gets around the difficulty with weak acids by postulating a non-electrolytic plus an electrolytic dissociation. This, however, would play havoc with the freezing-point determinations, and consequently the author makes the somewhat unintelligible assumption that "in the ordinary dissociation, the rotating motion of the ions is increased, but not the translatory motion ; the ions therefore rotate more vigorously after the dissociation, but the term RT which is decisive for the osmotic pressure, is not affected thereby. In the electrolytic dissociation, on the other hand, where the ions are separated, they cannot rotate around each other ; the translatory motion is increased and the term RT varies in a way that is determined by the degree of dissociation." *W. D. B.*

The relation between osmotic work and osmotic pressure. *C. Dieterici. Zeit. phys. Chem.* 29, *139* (*1899*). —The author points out that it is unnecessary for Noyes to worry over the change of concentration produced by pressing out of the solution the amount of solvent in which one reacting weight of the solute is dissolved, provided one takes the volume of the solution infinitely large. He also makes independently the objection already raised by Speyers against Noyes's putting the semipermeable membrane at the top of the tube, namely that it is unrealizable experimentally. *W. D. B.*

On the theory of solutions. *W. Kistiakowsky. Jour. Russ. Soc.* 30, *576* (*1898*). —The author gives vent to some views he holds in regard to solutions, osmotic pressure and work, and heat of dilution, and with comparative disregard of any experimental evidence, arrives at the following conclusion. Osmotic pressure may be observed in gases as well as in solutions. Semipermeable membranes both for gases and solutions consist of bodies that dissolve the substances that pass through them, and do not dissolve substances not passing through them. The possibility of determining theoretically the value of osmotic work is due to the continuity of the gaseous and liquid states. In cases where the law of Henry-Dalton is applicable, osmotic work assumes the simple expression $qO = RT$, but where it does not apply the expression becomes $qO = RT + K$. (q is osmotic pressure, O 'osmotic volume', R the gas constant, T the temperature, and K the heat of dilution.) *C. E. L.*

Velocities

Experiments on the decomposition of the halogen derivatives of benzene. *R. Löwenherz. Zeit. phys. Chem.* 29, *401* (*1899*). — The investigation includes determinations of the velocity with which chlor-, brom-, and iodo-benzene are decomposed by sodium amylate in amyl alcohol. Experiments were made at 50° and 125° ; for the higher temperature the author used an Ostwald thermostat filled with paraffin and provided with a regulator containing mixed aromatic hydrocarbons of b. p. 160°–170°.

The results are not very concordant. It was found that the presence of air increased the velocity of the reaction, and this is no doubt one of the principal causes of the variations observed.

In a current of air iodo-benzene was found to be decomposed 310 times faster than brom-benzene, and the latter 550 times faster than chlor-benzene. Brom-benzene itself was decomposed 230 times faster in a current of air than in a closed vessel. As regards temperature differences, it was found that brom-benzene in a current of air was decomposed only 9 times as fast at 125° as at 50°. Since the conditions of the reaction are so little understood, the results, while interesting, have scarcely more than a qualitative value. *A. P. S.*

On the velocity of electrical reaction, II. *E. Cohen. Proc. Roy. Acad. Amst.* 1899, *417.* — In this paper, the second of a series on electrical reaction velocity (3, 425), the author studies a Clark cell considered alone as a transition cell. The reaction occurring in such a cell, when the electrodes are connected by a short thick wire, is

$$\mathrm{Zn} + \mathrm{Hg_2SO_4} \rightleftarrows \mathrm{Hg_2} + \mathrm{ZnSO_4}.$$

If it were not for polarization the velocity constant K would be represented by

$$K = \frac{E}{R},$$

where R is the resistance of the cell. As it is impossible to realize this condition in a Clark cell when short-circuited, the author measures the specific resistance of zinc sulfate solutions of different strengths, and expresses the velocity constant as

$$K_1 = \frac{E}{\Omega}$$

where Ω is the measured specific resistance for the concentration producing the electromotive force E. Taking Jaeger's results for the change of the E. M. F. of a Clark cell above and below 39°, the author works out K_1 for different temperatures for both the stable and metastable phase of the salt, and represents the results in the plot of K_1 as a function of temperature. This shows that the velocity of reaction at 39° is the same for both the hepta- and hexahydrate, but that below 39° the reaction velocity for the metastable phase is slower than for the stable. *H. T. B.*

On velocity of crystallization. *G. Tammann. Zeit. phys. Chem.* 29, *51* (*1899*). — The aim of the investigation is shown in the following statements: It is well known that the linear velocity of crystallization increases at first with increased supercooling, reaches a maximum at about 20° of supercooling, beyond which it becomes independent of the supercooling. Although both the development of crystals not parallel to the surface of the crystallization tube, and the presence of foreign substances, affect the velocity of crystallization, these do not afford a sufficient explanation, and there must be still an important cause preventing the maximum velocity from manifesting itself at any supercooling of less than 20°. This cause is to be found in the slowness of the heat conduction away from the surface of crystallization.

To test this hypothesis, Tammann constructed an apparatus provided with a copper cylinder, as heat conductor, placed axially in the tube in which the experiment was to be performed. The results show that with this apparatus the velocity of crystallization increases more rapidly with increasing supercooling than when no copper cylinder is used. The substances employed were benzophenone and salol. The paper contains also a chapter on the latent heat of fusion and specific heat of benzophenone, apiol, and betol.

The results are:

	L h fusion	Sp h		
Apiol (m p 29.26°)	25.8 cal	cryst	0.300	(0–20°)
		liquid	0.382	"
Benzophenone (m p 48.5°)	23.4 cal	cryst	0.271	"
		liquid	0.369	"
Betol (m p 93°)	18.0 cal	cryst	0.299	(20–80°)
		"	0.260	(20–50°)
		"	0.217	(0–20°)
		liquid	0.338	(20–80°)
		"	0.273	(0–20°)

These results show a decreasing difference in the specific heat of liquid and solid betol with rising temperature; as the opposite was to be expected (Cf. Wied. Ann. 67, 871 (1899)), Tammann thinks it possble that there may here be an experimental error.

The concluding part is devoted to an investigation of the various modifications of benzophenone (3), apiol (2), salol (3), and betol (4). *A. P. S.*

On the speed of crystallization. *A. Bogojawlensky. Jour. Russ. Soc.* 30, *1041* (*1898*). — Reviewed (3, 424) from Zeit. phys. Chem. 27, 585 (1898).

Catalytic action of some metals on solutions of oxalic acid. *O. Sulc. Zeit. phys. Chem.* 28, *719* (*1899*). — Finely divided copper, silver, platinum, and palladium accelerate the decomposition of oxalic acid solutions in sunlight, copper being the least and palladium the most effective. Palladium also acts to a certain extent in the dark. *W. D. B.*

Electromotive Forces

Electrometric determinations of structure formulas. *R. Kieseritzky. Zeit. phys. Chem.* 28, *385* (*1899*). — The author has measured the potential difference of mercury salts of organic nitrogen compounds against a decinormal calomel electrode and draws conclusions from these data as to the concentration of mercury as ion in the solutions. The carboxyl mercury compounds show, as was to be expected, the highest concentration of mercury as ion. The concentration as ion in solutions of the amido-compounds turns out to be much higher than in solutions of imido compounds and therefore electrometric determinations can serve as a means of distinguishing between these two groups. Mercury glycocoll is an amido compound; mercury cyanid an imido compound. *W. D. B.*

Studies of some iodin compounds. *E. C. Sullivan. Zeit. phys. Chem.* 28, *523* (*1899*). — The author sums up his results somewhat as follows:

From measurements on conductivity and on rate of saponification it was found that diphenyliodonium hydroxid is one of the strong bases. The index of refraction R_D for iodin is 25.9 in phenyliodid, 28.3 in iodin as ion, and 27.9 in diphenyliodonium, 36.8 in $C_6H_5ICl_2$, and probably less than 22.9 in the iodates.

The electrical potential of chlorin is somewhat higher than that of $C_6H_5ICl_2$. On calculating the equilibrium constant from the electrical measurements, it appeared that chlorin in aqueous hydrochloric acid followed Henry's law.

The identity of the values of the electrical potential for solutions of ICl, RbClICl, and RbCl + ICl in hydrochloric acid points to the presence of the same electrically active constituent in the three cases. The reduction process is univalent.

Cryoscopic and conductivity measurements point to the existence of a complex ion in solutions of RbClICl and of ICl in aqueous hydrochloric acid.

W. D. B.

On electrolytic evolution of gas. *W. A. Caspari. Zeit. Elektrochemie*, 6, *37 ; Zeit. phys. Chem.* 30, *89* (*1899*). — The author sums up his results as follows :

A visible electrolytic evolution of hydrogen and oxygen takes place on platinized electrodes in acid solutions in atmospheric pressure and ordinary temperature under an electromotive force of 1.55–1.66 volt.

The electrolytic evolution of hydrogen on platinized electrodes is practically reversible. With other metals an excess voltage is necessary, making the phenomenon irreversible.

This excess voltage increases with the current density, but is practically independent of the state of the electrode surface. The value of the excess voltage is an important factor in the evolution of hydrogen due to chemical action.

Bromin and iodin precipitate reversibly on platinum. Silver precipitates reversibly from solutions of complex salts in spite of its low concentration as ion.

W. D. B.

Galvanic polarization in solutions of sulfates of the alkalies. *H. Jahn. Zeit. phys. Chem.* 29, *77* (*1899*). — The polarization of platinum electrodes dipping into *n*/8 solutions of Na_2SO_4, Li_2SO_4, and $(NH_4)_2SO_4$ was determined at 0° and at 40° from the thermal changes of the polarizing battery, which was placed in an ice calorimeter. The polarization was found to be a function of the intensity of the current used and so dependent upon the difference of potential between the electrodes of the electrolytic cell. The results obtained agree well with those calculated from the formula : $p = \phi + y \log_{10} I$, where p is the E. M. F. of polarization, ϕ a function of the intensity of the current, y a proportionality constant, and I the intensity of the current used.

L. K.

On the thermodynamics of thermocouples. *C. Liebenow. Wied. Ann.* 68, *316* (*1899*). — Contrary to the ideas of Clausius, Thomson, and Boltzmann, that heat conduction in a thermocouple plays no or only a very small part in the development of a thermoelectric current, the author considers that a thermoelectric force is inseparably bound with a flow of heat in a metal. He considers also that the passage of an electric current through a metal also gives rise to the flow of heat which can be made to flow from a low to a high temperature. From this point of view the author considers thermoelectric force as well as the Peltier and Thomson effects.

H. T. B.

On the charge of electricity carried by the ions produced by Röntgen rays.

J. J. Thomson. Phil. Mag. 46, *528* (*1898*). — The experiments described in this paper were undertaken to determine the magnitude of the charge of electricity carried by gaseous ions produced by Röntgen rays. Under a known E. M. F. the current passing through a gas, under the influence of the rays, gives a measure of the product

$$n\,e\,v,$$

where n is the number of ions in unit volume of gas, e the charge on an ion, and v the velocity of the positive and negative ions. The value of v being already known from Rutherford's experiments, it becomes necessary only to measure n to find e.

The method used by the author to find n depends on the results of Wilson, which are that when Röntgen rays pass through dust-free air, a cloud is produced by a sudden expansion. No cloud, or only a faint cloud, is produced when the rays are not passing. As a charged ion forms a nucleus for the condensation of a small drop of water, it is necessary only to know the size of the drops and the mass of water deposited per unit of volume to determine the number of drops and the number of ions in unit volume of the gas. After some trouble in finding a method to measure the size of the drops, the one finally selected was to observe the rate at which the cloud produced by the expansion sank and then to determine the radius from the formula

$$v = \frac{2}{9}\,\frac{ga^2}{\mu}$$

where v is the velocity of fall, a is the radius of the drops, and μ is the coefficient of viscosity. The fundamental points settled by the author were that the drops formed were deposited around the ions, giving the *ga* its electrical conductivity, and that the cloud produced by the expansion caught all the ions. The electrical measurements consisted in finding the rate of leak, on an electrometer, through the gas, when the rays were turned on. If the change in potential is V per sec. and the capacity of the system C include discharging vessel, connecting wires and quadrants of the electrometer, then the quantity of electricity flowing across the cross-section of the vessel is CV. This is equal to

$$n\,e\,u_0\,\mathrm{E\,A},$$

where u_0 is the mean velocity of the positive and negative ions, E the potential gradient, and A the area of the plates. From a study of the connection between the velocity and size of the drops, the number of ions in 1 cc of the gas before expansion is 2.94×10^4, which would give the number before expansion 4×10^4.

Correcting for the presence of a small cloud before the rays are turned on, and for the conductivity of the moist walls of the vessel, the ionic charge

$$e = 6.5 \times 10^{-10}$$

in electrostatic units. Experiments in air and hydrogen show that the charge is the same.

The most suggestive part of the paper, perhaps, is that, as the author points out, this charge is very nearly the same as the charge of the hydrogen ion in electrolysis, and indicates a close similarity. (See review of Townsend's paper on the Diffusion of Ions into Gases.) *H. T. B.*

The diffusion of ions into gases. *J. S. Townsend. Phil. Trans.* 193, *129* (*1899*). —The present paper is an exceedingly interesting and important one as illustrating the immense advance that has been made during the last year or so in the domain of molecular physics. In the light of the modern ideas relating to the molecular conductivity of gaseous ions and a mathematical analysis of the interdiffusion of two gases passing through a tube capable of absorbing one of them, the author determines the diffusion coefficients of the ions for several gases. The general theory of his method is that if a small quantity of one gas A is mixed with another gas B and the two passed through a tube, the walls of which absorb A, then the amount of the gas A removed from the mixture will depend on its rate of diffusion. Subjecting a gas to the influence of the Röntgen rays under a steady difference of potential the charged ions are passed through a number of equally sized brass tubes arranged parallel to one another systematically around a brass disc. After passing through these tubes the gas is passed over an electrode connected with the quadrants of an electrometer. By suitably arranging the difference of potential and the length of the metal tubes and correcting for the number of recombinations between the positive and negative ions in the gas itself, the diffusion coefficient may be calculated by the loss in conductivity of the gas due to the absorption of the ions by the metal tubes. Either positive or negative ions could be absorbed, depending on the polarity of the absorbing electrode. Determining this diffusion coefficient for air, oxygen, hydrogen, and carbon dioxid, the author goes on to show that if N is the number of molecules in one cc of a gas at atmospheric pressure and 15° C and e is the ionic charge, then Ne for

Air - - - - - -	1.35×10^{10}	electrostatic units
Oxygen - - - - -	1.25×10^{10}	" "
Carbonic acid - - -	1.30×10^{10}	" "
Hydrogen - - - -	1.00×10^{10}	" "

Electrolytic experiments show that if E is the charge on a hydrogen atom and N the number of molecules in one cc of hydrogen gas evolved by one electromagnetic unit of electricity, then

$$NE = 1.22 \times 10^{10} \text{ electrostatic units,}$$

which stands in remarkable agreement with the mean value for the different gases. Taking the value for the charge on an ion to be 6×10^{-10}, which appears to be the same for the gaseous as well as the electrolytic ion, then the weight of a hydrogen molecule is found to be

$$4.5 \times 10^{-24} \text{ gram.}$$

From a comparison of the rates of diffusion of the ions with the rates of interdiffusion of gases and vapors, the radius of an ion in hydrogen is found to be

$$8.2 \times 10^{-8} \text{ cm,}$$

in oxygen

$$9.2 \times 10^{-8} \text{ cm.}$$

H. T. B.

Electrolysis and Electrolytic Dissociation

Source of error in the electrolytic estimation of iron. *S. Avery and B.*

Dales. Ber. chem. Ges. Berlin, 32, 640 (*1899*). — The authors had examined the composition of the deposit formed in estimating iron electrolytically according to Classen's method. They find the iron contains from 0.15 to 0.5 percent carbon; with Smith's method 1.2–5.0 percent, and with Moore's method 0.2–0.5 percent. The latter precipitate contains phosphorus. *C. G. L. W.*

An electrolytic current interrupter. *A. Wehnelt. Wied. Ann.* **68**, *233* (*1899*). — The author describes with great care the use of the now famous electrolytic break that bears his name. By repeating the experiments of Lagrange and Hoho, and those of Richarz, he was led to try the effect of the use of a very small and a very large electrode in dilute sulphuric acid as a current interrupter for an induction coil. The larger electrode was made from a strip of lead, and the smaller one a platinum point. The remarkable effect produced showed at once the utility of the arrangement, and the great superiority over the mechanical breaks hitherto in use. His first arrangement made the small or "active electrode" negative, but on increasing the voltage to about 110 the platinum melted. By making the active electrode positive a much better effect was produced on the induction coil, and up to a voltage of 220 the platinum point did not melt. A study of the influence of induction in the circuit on the break showed that where the active electrode is positive it conditions the number of interruptions, as shown by the change in tone. The current strength increases with the surface of the active electrode, but not proportionally. The current density on the electrode requires to reach a critical value before the interruptions commence. Induction free resistance in the circuit serves to lessen the number of interruptions only by lowering the voltage. Interruptions as high as 2200 per second were measured. The lowest voltage to produce effective breaks was found to be 12. The break works well for alternating currents and especially when, instead of a lead plate, an aluminium plate be used, as in the Grätz cell. This stops altogether the phase making the active electrode negative. The density of the sulphuric acid to produce the best results was found to be from 1.16 to 1.20. Calorimetric measurements of the energy lost in the interrupter showed from 30 to 80 percent, but is of the same order as in the older forms. An examination of the effect on the active electrode showed that it is surrounded by a covering of glowing gas, which suddenly explodes, thus completely interrupting the current. A return of the electrolyte around the electrode starts the current again. An examination of the gas developed shows it to be made up of an explosive mixture of oxygen and hydrogen, with the former gas predominating. A careful examination was made of current curves by means of a Braun tube and rotating mirror. The sudden rise and absolutely sharp break is at once seen, and shows wherein the great value of the interrupter lies. The reactionary influence of the secondary coil of an induction coil for different spark gaps is clearly shown. The influence of a condenser across the break shows an increase in the maximum amplitude of the current curve. By introducing self-induction and capacity both it was found possible to change the current curve very considerably. The form of break made by enclosing the active electrode in a glass tube, with a narrow opening in the electrolyte, shows the same results, only the light effect hitherto seen on the active electrode, now appears in the narrow opening. With this form the polarity appears to be of no consequence. The objection to this arrangement is that a much higher voltage is required to produce the interruptions, and the glass around the opening soon disintegrates. The author concludes his paper by giving the best method of construction and the various applications to which the break can obviously be put. *H. T. B.*

On the action in the Wehnelt electrolytic interrupter. *A. Voller and B. Walter. Wied. Ann.* **68**, *526* (*1899*).—There is very little new in the present paper. The authors consider an anomalous electrolysis to take place in the Wehnelt cell, and show its presence by the development of a much larger quantity of gas on the small active electrode than should be produced according to Faraday's law. They vary the amount of gas considerably with the induction in the circuit, but do not give a satisfactory explanation of the phenomenon. The development of a pure metal spectrum in the glowing gas around the small electrode is pointed out, and they suggest this method with different metals as electrode, for producing pure spectra of the different metals. As might be expected, the authors find the interrupter absorbs more energy than the older forms, which they had previously taken so much trouble to study. *H. T. B.*

A research with the Wehnelt interrupter. *E. Lecher. Wied. Ann.* **68**, *623* (*1899*).—As the sparks produced in an induction cell by a Wehnelt break resemble very nearly an electric arc, the author studies the influence of a magnetic field on them. He obtains some very interesting results, showing that the sparks may be rotated in a magnetic field. He points out that the sparks have a definite current direction and correspond to the break of the primary current, and that no effect is produced on closing that current. *H. T. B.*

Dependence of the transference number on the nature of the membrane separating the solutions. *W. Bein. Zeit. phys. Chem.* **28**, *439* (*1899*).—Porous plates change the transference numbers but slightly. All other membranes have a marked effect, decreasing the transference number of the cation. For instance, with hydrochloric acid the author finds 0.167 for the transference number of chlorin, when a porous plate was used, 0.176 with parchment paper, 0.29 with fish-bladder, 0.29 with gold beater's skin. Using porous plates, a value of 0.601 was obtained for sodium chlorid, while the value was about 0.73 when using gold beater's skin. *W. D. B.*

On a remarkable class of inorganic acids and the electrolytic behavior thereof. *W. Hittorf and H. Salkowski. Zeit. phys. Chem.* **28**, *546* (*1899*).—Anhydrous platinum chlorid and anhydrous gold chlorid when dissolved in water form complex acids in which the gold and platinum are present in the anions. The authors assume that they are dealing with the dibasic acid H_2PtCl_4O and the monobasic acid $HAuCl_3OH$. The reason for not making the latter acid dibasic is that this would make the transference number for the anion 0.227, which is remarkably high, especially in view of the fact that the transference for the platinum acid is 0.126 on the assumption of dibasicity.

W. D. B.

On the conductivity of a mixture of electrolytes. *F. Barmwater. Zeit. phys. Chem.* **28**, *424* (*1899*).—For mixture of two electrolytes, the author deduces the expression

$$1 - x_1 = k_1 \sqrt[3]{m_1 + m_2}$$
$$1 - x_2 = k_1 \sqrt[3]{m_1 + m_2},$$

where m_1 and m_2 are the concentration in gram equivalents per liter, while x_1 and x_2 are the fractional dissociations. The formulas apply fairly well to mixtures of NaCl and KCl, of NaCl and KI, of NaCl and KNO_3, of KCl and KNO_3.

W. D. B.

On the cause of the change in the conductivity of a metal powder. *T. Sundorph. Wied. Ann.* 68, *594* (*1899*). — By placing iron or nickel filings between two metal plates in series with a battery and galvanometer, the author points out how strongly the filings can be made to conduct the electric current by simply short-circuiting them a number of times with a wire. The conductivity is destroyed by tapping on the plates. The only explanation the author considers adequate is the temporary welding together of the metal particles by the sparks produced on breaking the short-circuit. Two examples are given in support of this explanation. Aschkinass' coherer theory is briefly referred to.

H. T. B.

Dielectricity and Optics

Dielectric constants and changes of aggregation of alcohols at low temperatures. *R. Abegg and W. Seitz. Zeit. phys. Chem.* 29, *242* (*1899*). — The dielectric constants of amyl, isobutyl, propyl, ethyl, and methyl alcohols and also of nitrobenzene were determined at temperatures varying from that of the room down to their points of solidification. The results agree tolerably well with those calculated according to the formula $-\frac{dD}{dT} = \frac{1}{190}$ D which equals $D = Ce^{T/190}$, where C is a constant (i. e. D for T = o).

The measurements were made with Nernst's apparatus. The temperatures were obtained by using the following baths: water 16°, snow 0°, boiling ammonia − 34°, carbon dioxid and ether − 80°, sodium chlorid cryohydrate − 21.3°, melting chloroform − 67°, melting toluene − 102°, melting ether − 117.6, and melting ethyl bromid − 125.9°.

Methyl alcohol remains mobile down to its freezing-point; the other alcohols become more and more viscous until they finally solidify to a glassy mass. The specific gravity of solid alcohols is higher than that of the respective liquids. The glassy amorphous alcohols in some cases changed to the crystalline form, however, without causing a change in the dielectric constant. The latter changes suddenly become very small when the alcohols pass from the liquid to the solid state. The results do not agree with those calculated from the refraction formulas.

As the dielectric constants of ether and benzene (which are non-associated liquids) vary with the temperature very much, the same as do those of the alcohols, the authors conclude that the increase of the dielectric constants of the latter substances with decrease of temperature is probably not due to the polymerization.

L. K.

The dielectric behavior of a crystalline liquid. *R. Abegg and W. Seitz. Zeit. phys. Chem.* 29, *491* (*1899*). — The dielectric constant of *p*-oxyanisol shows no sudden change when the crystalline liquid appears at 134°; while there is a marked variation when the solid phase appears at 93°.

W. D. B.

Relation between dissociating force, dielectric constant, and molecular state of liquids. *H. Euler. Zeit. phys. Chem.* **28**, *619* (*1899*). — The general results are that polymerized substances usually have high dielectric constants. On the other hand, there are 'normal' liquids with high dielectric constant and marked dissociating power, while there are some polymerized liquids with low dielectric constant and no dissociating power. Solutions with benzonitrile as solvent show a decreasing molecular conductivity with increasing dilution. [Similar cases have been observed by Kahlenberg.] *W. D. B.*

Studies on electrical oscillations, II. *H. Kauffmann. Zeit. phys. Chem.* **28**, *673* (*1899*). — The presence of an easily broken bond is characteristic of substances which absorb electrical oscillations of about 75 cm wave-length. The degree to which the phenomenon takes place depends essentially on the constitution of the reacting substances, and the author points out the comparative effects of different groups. *W. D. B.*

Refraction indices for pure water and normal salt solutions. *C. Bender. Wied. Ann.* **68**, *343* (*1899*). — The present paper is a continuation of a previous paper by the author in which he determined the refraction indices for a number of salt solutions. In order to apply certain corrections to the results to reduce to a standard temperature, he undertakes to study the variation with temperature. This paper contains the results for pure water, using the Pulfrich refractometer and a simple constant temperature device. Great care was taken to have the liquid and the glass prism at the same temperature. The author finds that for each of the hydrogen lines H_α, H_β, and H_γ the refraction index may be expressed as a simple parabolic function of the temperature instead of a linear function, as was shown by Wüllner. It is also shown that the refraction index for air-free water is the same as for water containing air between 10° and 40° C. Further results are promised in a later paper. *H. T. B.*

The phase change of light reflected from mercury. *H. Wallbott. Wied. Ann.* **68**, *471* (*1899*). — The author adopts the method of Wernicke and as a thin plate uses mica, collodium, glass or gelatin. Most of the results were obtained with mica. By a simple method of lightly silvering the surface of the plates he was able to work with thicknesses of 4 wave-lengths, whereas formerly plates of 9 wave-lengths had to be used. Only half of the plate was covered with mercury, so that by means of a spectrometer the interference bands produced by the reflection of the light with and without the mercury were compared at the same time. This gave the change of phase due to the mercury. A small decrease in the phase acceleration was noticed towards the violet end of the spectrum. Taking the four Traunhofer lines C, D, E, F the following measurements for the acceleration in phase were obtained:

	C	D	E	F
Wave-length - - - -	656	589	527	486
Acceleration - - - -	0.417	0.413	0.405	0.395

The theory of the phase change of liquid reflected from metal surfaces was found to agree well with the experiments from thick mercury surfaces.

H. T. B.

ON THE EMISSION AND ABSORPTION OF WATER VAPOR BY COLLOIDAL MATTER

BY P. DUHEM

INTRODUCTION

In writing my first memoir *On permanent deformations and hysteresis*,[1] I introduced a chapter entitled: *Application of the preceding theory to changes of physical state*, and wrote at the beginning of this chapter, the following sentence: "This chapter is reduced almost to its title; nevertheless I believe that the application of the preceding theory to changes of physical state will be, in the future, fertile in results; many of the phenomena of false equilibrium which are mysteries to-day will, no doubt, be explained and classified by means of the principles which I have indicated."

The experiments of Gernez on the different modifications of sulphur,[2] which were carried out at great length and with much care not long after, were found to agree even in the most minute details with the principles above mentioned. My attention was drawn, later on, to the remarkable researches of Barus and Strouhal upon the tempering and annealing of steel; these authors had, earlier than myself, regarded the phenomena of tempering and annealing as physico-chemical changes under hysteresis; my theory, when applied to their observations, was found to accord exactly with them.[3] While studying this

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[1] Mém. Acad. Roy. Belg. 44, (1896).

[2] Ibid; also Zeit. phys. Chem. 23, 193 (1897).

[3] Mém. Acad. Roy. Belg. 46 (1898).

case, I had occasion to advance certain ideas which seem destined to play an important part in the study of permanent changes of physical or chemical state; I refer in particular to the idea of the *region of secular variations.*

This conception has made it possible to offer an explanation of the curious properties of irreversible nickel steels, discovered and studied by C. E. Guillaume.[1] The theoretical study of systems which depend upon a single variable under hysteresis, is comparatively simple; but it becomes much more complex where there are two variables affected by hysteresis. On the other hand, if the coefficient of hysteresis is small for one or for both of these variables, then it is possible, in studying the system, to make use of certain very convenient approximation theorems. My aim in establishing these theorems[2] was to make possible an analysis of the complex phenomena presented by the expansion of glass, which were at that time being carefully studied by L. Marchis. The methods indicated were developed and applied by Marchis,[3] and they enabled him to coordinate a mass of observations which would otherwise have formed a perfect chaos. These various researches have already transformed the study of changes of physical state or of chemical constitution, affected by hysteresis, into a logical system.

Some extremely important work, carried on for several years, and published almost immediately after the appearance of my first theoretical papers, seems to me to contribute a new chapter to the subject in hand. I refer to the admirable experiments of van Bemmelen[4] on the hydration and desiccation of colloidal jellies. On studying the changes which occur in substances like gelatinous silica or colloidal ferric oxide when placed in an atmosphere of water vapor, the hysteresis which affects these physico-chemical changes becomes evident; and van Bemmelen deduced from this hysteresis certain complex laws.

The principles before mentioned, which have already received

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[1] Mém. Soc. Sci. phys. nat. Bordeaux (5) 4, 452 (1898).

[2] Mém. Acad. Roy. Belg. 46 (1898).

[3] Mém. Soc. Sci. phys. nat. Bordeaux (5) 4, 1 (1898).

[4] Zeit. anorg. Chem. 13, 233 (1896); 18, 14 and 98 (1898); 20, 185 (1899).

frequent application, seem applicable also to the interpretation of the experimental laws laid down by van Bemmelen, and to the uniting of them with those which have been discovered in the study of changes of different kinds, — elastic deformations, magnetization, — as well as of the physico-chemical changes of state. The application of this theory of hysteresis to the laws established by van Bemmelen is the object of the present memoir.

CHAPTER I

PHENOMENA OF INCIPIENT DEHYDRATION

1. Formulation of the problem of the absorption of water vapor by a body, when this absorption is accompanied by hysteresis

Let us assume that a certain substance is capable of hydration. At a certain stage, a mass m of the anhydrous substance will be combined with a mass hm of water, the mass of the hydrate being $(1 + h)m$. Let us suppose that for the definition of the state of this hydrate it is sufficient to know:

(1) its specific volume v;
(2) the value of h;
(3) the absolute temperature T.

The internal potential of the mass of hydrate $(1 + h)m$ will then have the form

$$m(1 + h)\,\mathfrak{F}(v, h, \mathrm{T}).$$

Now suppose that the hydrate coexists with a mass of water vapor, M, of which V is the specific volume, and of which the internal potential has the form

$$\mathrm{M}\,\mathfrak{G}(\mathrm{V}, \mathrm{T})\,;$$

and suppose, finally, that the system is under a normal and uniform pressure Π.

Then suppose the system to undergo a virtual isothermal change. In this change we shall have

$$dM = -m dh\,;$$

and the value of the uncompensated work will be

$$\begin{aligned} d\tau = &- m(1+h)\left(\frac{\partial \mathfrak{F}}{\partial v} + \Pi\right)dv \\ &- M\left(\frac{\partial \mathfrak{G}}{\partial V} + \Pi\right)dV \\ &- m\Big[\mathfrak{F} + \Pi v + (1+h)\frac{\partial \mathfrak{F}}{\partial h} \\ &\qquad - \mathfrak{G} - \Pi V \Big]dh. \end{aligned} \tag{1}$$

If the system is subject neither to friction nor to hysteresis, this work must, in order that the initial state shall be a state of equilibrium, be equal to 0, whatever the values of dv, dV, dh. This gives the three equations of equilibrium:

$$\left.\begin{aligned} &\frac{\partial \mathfrak{F}(v,h,T)}{\partial v} = -\Pi, \\ &\frac{\partial \mathfrak{G}(V,T)}{\partial V} = -\Pi, \\ &\mathfrak{F}(v,h,T) + (1+h)\frac{\partial \mathfrak{F}(v,h,T)}{\partial h} - \mathfrak{G}(V,T) \\ &\qquad = -\Pi(v - V), \end{aligned}\right\} \tag{2}$$

which make it possible to find v, V, and h when the exterior pressure Π and the temperature T are given.

Suppose, however, that the hydration is subject to hysteresis. We shall then retain the first two equations (2):

$$\left.\begin{aligned} &\frac{\partial \mathfrak{F}(v,h,T)}{\partial v} = -\Pi, \\ &\frac{\partial \mathfrak{G}(V,T)}{\partial V} = -\Pi, \end{aligned}\right\} \tag{2 bis}$$

and replace the last by the following:

$$
\begin{aligned}
&\left[\frac{\partial \mathfrak{F}(v,h,\mathrm{T})}{\partial v} + (1+h)\frac{\partial^2 \mathfrak{F}(v,h,\mathrm{T})}{\partial v \partial h} + \Pi\right] dv \\
&\qquad - \left[\frac{\partial \mathfrak{G}(\mathrm{V},\mathrm{T})}{\partial \mathrm{V}} + \Pi\right] d\mathrm{V} \\
&+ \left[2\frac{\partial \mathfrak{F}(v,h,\mathrm{T})}{\partial h} + (1+h)\frac{\partial^2 \mathfrak{F}(v,h,\mathrm{T})}{\partial h^2}\right] dh \\
&+ \left[\frac{\partial \mathfrak{F}(v,h,\mathrm{T})}{\partial \mathrm{T}} + (1+h)\frac{\partial^2 \mathfrak{F}(v,h,\mathrm{T})}{\partial h \partial \mathrm{T}} - \frac{\partial \mathfrak{G}(\mathrm{V},\mathrm{T})}{\partial \mathrm{T}}\right] d\mathrm{T} \\
&\qquad + (v-\mathrm{V})\, d\Pi \\
&\qquad + f(v,\mathrm{V},h,\mathrm{T},\Pi)\,|dh| = 0, \qquad (3)
\end{aligned}
$$

where $|dh|$ represents the *absolute value* of dh. We will transform these relations in the following manner:

Solving the equations (2 bis) for v and V, we find

$$
\left.
\begin{aligned}
v &= v(h,\Pi,\mathrm{T}), \\
\mathrm{V} &= \mathrm{V}(\Pi,\mathrm{T}).
\end{aligned}
\right\} \qquad (4)
$$

We will then set

$$
\left.
\begin{aligned}
\mathfrak{F}[v(h,\Pi,\mathrm{T}),h,\mathrm{T}] + \Pi v(h,\Pi,\mathrm{T}) &= \phi(h,\Pi,\mathrm{T}), \\
\mathfrak{G}[\mathrm{V}(\Pi,\mathrm{T}),\mathrm{T}] + \Pi \mathrm{V}(\Pi,\mathrm{T}) &= \Phi(\Pi,\mathrm{T}), \\
f[v(h,\Pi,\mathrm{T}),\mathrm{V}(\Pi,\mathrm{T}),h,\mathrm{T},\Pi] &= g(h,\Pi,\mathrm{T}).
\end{aligned}
\right\} \qquad (5)
$$

The first two equations (5) give us

$$
\begin{aligned}
\frac{\partial \phi(h,\Pi,\mathrm{T})}{\partial h} &= \frac{\partial \mathfrak{F}(v,h,\mathrm{T})}{\partial h} + \left[\frac{\partial \mathfrak{F}(v,h,\mathrm{T})}{\partial v} + \Pi\right]\frac{\partial v}{\partial h}, \\
\frac{\partial \phi(h,\Pi,\mathrm{T})}{\partial \Pi} &= v + \left[\frac{\partial \mathfrak{F}(v,h,\mathrm{T})}{\partial v} + \Pi\right]\frac{\partial v}{\partial \Pi}, \\
\frac{\partial \phi(h,\Pi,\mathrm{T})}{\partial \mathrm{T}} &= \frac{\partial \mathfrak{F}(v,h,\mathrm{T})}{\partial \mathrm{T}} + \left[\frac{\partial \mathfrak{F}(v,h,\mathrm{T})}{\partial v} + \Pi\right]\frac{\partial v}{\partial \mathrm{T}}, \\
\frac{\partial \Phi(\Pi,\mathrm{T})}{\partial \Pi} &= \mathrm{V} + \left[\frac{\partial \mathfrak{G}(\mathrm{V},\mathrm{T})}{\partial \mathrm{V}} + \Pi\right]\frac{\partial \mathrm{V}}{\partial \Pi}, \\
\frac{\partial \Phi(\Pi,\mathrm{T})}{\partial \mathrm{T}} &= \frac{\partial \mathfrak{G}(\mathrm{V},\mathrm{T})}{\partial \mathrm{T}} + \left[\frac{\partial \mathfrak{G}(\mathrm{V},\mathrm{T})}{\partial \mathrm{V}} + \Pi\right]\frac{\partial \mathrm{V}}{\partial \mathrm{T}}.
\end{aligned}
$$

In these relations we have set, for brevity, v, V, in place of $v(h, \Pi, T)$, $V(\Pi, T)$.

But the equations (4) transform the equations (2 bis) into identities, and we have

$$\left.\begin{aligned} \frac{\partial\phi(h, \Pi, T)}{\partial h} &= \frac{\partial\mathfrak{F}(v, h, T)}{\partial h}, \\ \frac{\partial\phi(h, \Pi, T)}{\partial\Pi} &= v, \\ \frac{\partial\phi(h, \Pi, T)}{\partial T} &= \frac{\partial\mathfrak{F}(v, h, T)}{\partial T}, \\ \frac{\partial\Phi(\Pi, T)}{\partial\Pi} &= V, \\ \frac{\partial\Phi(\Pi, T)}{\partial T} &= \frac{\partial\mathfrak{G}(V, T)}{\partial T}. \end{aligned}\right\} \qquad (6)$$

The first of the equations (6) gives, in turn, the equations:

$$\frac{\partial^2\phi(h, \Pi, T)}{\partial h^2} = \frac{\partial^2\mathfrak{F}(v, h, T)}{\partial h^2} + \frac{\partial^2\mathfrak{F}(v, h, T)}{\partial v\partial h}\frac{\partial v}{\partial h},$$

$$\frac{\partial^2\phi(h, \Pi, T)}{\partial h\partial T} = \frac{\partial^2\mathfrak{F}(v, h, T)}{\partial h\partial T} + \frac{\partial^2\mathfrak{F}(v, h, T)}{\partial v\partial h}\frac{\partial v}{\partial T}.$$

But the first equation (2 bis) gives by differentiation

$$\frac{\partial^2\mathfrak{F}(v, h, T)}{\partial v\partial h} = 0, \qquad (7)$$

whence the preceding equations become

$$\left.\begin{aligned} \frac{\partial^2\phi(h, \Pi, T)}{\partial h^2} &= \frac{\partial^2\mathfrak{F}(v, h, T)}{\partial h^2}, \\ \frac{\partial^2\phi(h, \Pi, T)}{\partial h\partial T} &= \frac{\partial^2\mathfrak{F}(v, h, T)}{\partial h\partial T}. \end{aligned}\right\} \qquad (8)$$

In virtue of equations (2 bis), (5), (6), (7), and (8), the equation (3) becomes simply:

$$\begin{aligned}&\frac{\partial}{\partial h}\left[\phi(h,\Pi,\mathrm{T}) + (1+h)\frac{\partial\phi(h,\Pi,\mathrm{T})}{\partial h}\right]dh\\
&+\frac{\partial}{\partial \mathrm{T}}\left[\phi(h,\Pi,\mathrm{T}) + (1+h)\frac{\partial\phi(h,\Pi,\mathrm{T})}{\partial h} - \Phi(\Pi,\mathrm{T})\right]d\mathrm{T}\\
&+\frac{\partial}{\partial \Pi}\left[\phi(h,\Pi,\mathrm{T}) + (1+h)\frac{\partial\phi(h,\Pi,\mathrm{T})}{\partial h} - \Phi(\Pi,\mathrm{T})\right]d\Pi\\
&\qquad\qquad + g(h,\Pi,\mathrm{T})\,|dh| = 0. \qquad (9)\end{aligned}$$

This equation is of the type, often discussed in previous papers, which governs the permanent changes in a system where only one variable is subject to hysteresis.

We shall study, in particular, the case where the temperature is maintained practically constant; hence we shall suppress, in equation (9), the term in $d\mathrm{T}$; indeed, we need not make any explicit use of the letter T, which represents a simple constant.

If we take the pressures Π as abscissae and the degrees of hydration h as ordinates, every realizable trajectory will be composed of *ascending segments* which satisfy the differential equation

$$\begin{aligned}&\left\{\frac{\partial}{\partial h}\left[\phi(h,\Pi) + (1+h)\frac{\partial\phi(h,\Pi)}{\partial h}\right] + g(h,\Pi)\right\}dh\\
&+\frac{\partial}{\partial \Pi}\left[\phi(h,\Pi) + (1+h)\frac{\partial\phi(h,\Pi)}{\partial h} - \Phi(\Pi)\right]d\Pi = 0, \qquad (10)\end{aligned}$$

and which are connected by *descending segments* which satisfy the differential equation

$$\begin{aligned}&\left\{\frac{\partial}{\partial h}\left[\phi(h,\Pi) + (1+h)\frac{\partial\phi(h,\Pi)}{\partial h}\right] - g(h,\Pi)\right\}dh\\
&+\frac{\partial}{\partial \Pi}\left[\phi(h,\Pi) + (1+h)\frac{\partial\phi(h,\Pi)}{\partial h} - \Phi(\Pi)\right]d\Pi = 0. \qquad (10\,\text{bis})\end{aligned}$$

The ascending and descending lines passing through any same point (h, Π) intersect, in general, at a certain angle; they are tangent to each other at every point along the *line of natural states*

$$g(h,\Pi) = 0. \qquad (11)$$

It is one of our postulates that the isothermal changes in the system shall be subject to the law of the displacement of equilibrium by change of pressure; and we note that, since the transfer, at constant temperature and pressure, of a mass of water from the vapor to the hydrate is necessarily accompanied by a diminution of volume, it is plain that in the equations (10) and (10 bis), dh and $d\Pi$ will have the same sign.

Let $V(\Pi)$ be the specific volume of the water vapor, and $v(h, \Pi)$ that of the hydrate, at the temperature in question. Then we have

$$\frac{d\Phi(\Pi)}{d\Pi} = V(\Pi),$$

$$\frac{\partial\Phi(h, \Pi)}{\partial\Pi} = v(h, \Pi);$$

and, consequently,

$$\frac{\partial}{\partial\Pi}\left[(\phi(h, \Pi) + (1 + h)\frac{\partial\phi(h, \Pi)}{\partial h} - \Phi(\Pi)\right]$$

$$= v(h, \Pi) + (1 + h)\frac{\partial v(h, \Pi)}{\partial h} - V(\Pi), \tag{12}$$

an equation which then necessitates the inequality

$$\frac{\partial}{\partial\Pi}\left[\phi(h, \Pi) + (1 + h)\frac{\partial\phi(h, \Pi)}{\partial h} - \Phi(\Pi)\right] < 0; \tag{13}$$

whence the preceding convention gives us the two inequalities

$$\left.\begin{aligned} \frac{\partial}{\partial h}\left[\phi(h, \Pi) + (1 + h)\frac{\partial\phi(h, \Pi)}{\partial h}\right] + g(h, \Pi) > 0, \\ \frac{\partial}{\partial h}\left[\phi(h, \Pi) + (1 + h)\frac{\partial\phi(h, \Pi)}{\partial h}\right] - g(h, \Pi) > 0. \end{aligned}\right\} \tag{14}$$

We will now put, for brevity,

$$F(h, \Pi, T) = \phi(h, \Pi, T) + (1 + h)\frac{\partial\phi(h, \Pi, T)}{\partial h} - \Phi(\Pi, T), \tag{15}$$

and we can then write the inequalities (13) and (14) in the forms

$$\frac{\partial F(h, \Pi, T)}{\partial \Pi} < 0, \qquad (13 \text{ bis})$$

$$\left.\begin{aligned} \frac{\partial F(h, \Pi, T)}{\partial h} + g(h, \Pi, T) > 0, \\ \frac{\partial F(h, \Pi, T)}{\partial h} - g(h, \Pi, T) > 0. \end{aligned}\right\} \qquad (14 \text{ bis})$$

These inequalities will be of service further on.

2. Establishment of the formula determining the velocity of hydration

Let us consider a system in which, to begin with, the temperature shall be considered rigorously constant; and suppose that between two succeeding instants, t_0, t_1, the pressure Π of the water vapor has undergone slight variations in both directions, passing between the values Π_0 and Π_1; h will have passed from the value h_0 to the slightly different value h_1; let us endeavor to determine the value of $(h_1 - h_0)$.

For each ascending element in the change, we may write, because of equations (10) and (15),

$$\left[\frac{\partial F(h, \Pi)}{\partial h} + g(h, \Pi)\right] dh + \frac{\partial F(h, \Pi)}{\partial \Pi} d\Pi = 0. \qquad (15)$$

We then add, member for member, all these equations, observing:

(1) that, in all of them, dh, $d\Pi$, are positive quantities;

(2) that h and Π always differ by very little from h_0 and Π_0.

The resulting equation, when only infinitesimals of the first order are considered, may be written:

$$\left[\frac{\partial F(h_0, \Pi_0)}{\partial h_0} + g(h_0, \Pi_0)\right] \sum_{+} dh + \frac{\partial F(h_0, \Pi_0)}{\partial \Pi_0} \sum_{+} d\Pi = 0, \qquad (16)$$

in which $\sum_{+} dh$ add $\sum_{+} d\Pi$ denote the sums of all the positive values of dh and $d\Pi$.

In the same way, for each descending element of the change, we may write, because of equations (10 bis) and (15):

$$\left[\frac{\partial F(h,\Pi)}{\partial h}-g(h,\Pi)\right]dh+\frac{\partial F(h,\Pi)}{\partial \Pi}d\Pi=0.$$

Adding these equations, member for member, and observing

(1) that, in all, dh and $d\Pi$ are negative,

(2) that h and Π differ by very little from h_0 and Π_0,

we may write the resulting equation, retaining infinitesimals of the first order only, in the form

$$\left[\frac{\partial F(h_0,\Pi_0)}{\partial h_0}-g(h_0,\Pi_0)\right]\sum_{-}dh+\frac{\partial F(h_0,\Pi_0)}{\partial \Pi_0}\sum_{-}d\Pi=0), \quad (16\text{ bis})$$

in which $\sum\limits_{-} dh$ and $\sum\limits_{-} d\Pi$ denote the sums of all the negative values of dh and $d\Pi$. Adding the equations (16) and (16 bis), member to member, and noting that we have

$$\left.\begin{aligned}&\sum_{+}dh+\sum_{-}dh=\sum dh=h_1-h_0,\\&\sum_{+}dh-\sum_{-}dh=\sum|dh|,\\&\sum_{+}d\Pi+\sum_{-}d\Pi=\sum d\Pi=\Pi_1-\Pi_0,\\&\sum_{+}d\Pi-\sum_{-}d\Pi=\sum|d\Pi|,\end{aligned}\right\}\quad(17)$$

we find

$$\frac{\partial F(h_0,\Pi_0)}{\partial h_0}(h_1-h_0)+g(h_0\Pi_0)\sum|dh|+\frac{\partial F(h_0,\Pi_0)}{\partial \Pi_0}(\Pi_1-\Pi_0)=0. \quad (18)$$

On the other hand, if we multiply equation (16) by

$$\frac{\partial F(h_0\Pi_0)}{\partial h_0}-g(h_0,\Pi_0),$$

and equation (16 bis) by

$$\frac{\partial F(h_0,\Pi_0)}{\partial h_0}+g(h_0,\Pi_0),$$

and add the results, member to member, keeping in mind the equations (17), we get

$$\begin{aligned}&\left\{\left[\frac{\partial F(h_0, \Pi_0)}{\partial h_0}\right]^2-\left[g(h_0, \Pi_0)\right]^2\right\}(h_1-h_0)\\&+\frac{\partial F(h_0, \Pi_0)}{\partial h_0}\,\frac{\partial F(h_0, \Pi_0)}{\partial \Pi_0}(\Pi_1=\Pi_0)\\&=\frac{\partial F(h_0, \Pi_0)}{\partial \Pi_0}g(h_0, \Pi_0)\sum|d\Pi|.\end{aligned}\tag{19}$$

The projection, on the OΠ axis, of the representative point of the system has described, at least once, the segment comprised between the abscissæ Π_0 and Π_1, in such wise that $\Sigma\,|d\Pi|$ cannot be less than $|\Pi_1-\Pi_0|$. The path of this projection includes, besides the line between the abscissæ Π_0 and Π_1, certain portions of the OΠ axis traversed an even number of times; we will denote by 2λ the length of the path traversed by the projected point in describing these portions. We shall then have

$$\sum|d\Pi|=|\Pi_1-\Pi_0|+2\lambda.$$

Hence, equation (19) may be written in the form

$$\begin{aligned}h_1-h_0=&\frac{\dfrac{\partial F(h_0, \Pi_0)}{\partial \Pi_0}}{\left[\dfrac{\partial F(h_0, \Pi_0)}{\partial h_0}\right]^2-\left[g(h_0, \Pi_0)\right]^2}\left\{g(h_0\,\Pi_0)\,|\Pi_1-\Pi_0|\right.\\&\qquad\left.-\frac{\partial F(h_0, \Pi_0)}{\partial h_0}(\Pi_1-\Pi_0)\right\}\\&+\frac{2\dfrac{\partial F(h_0, \Pi_0)}{\partial \Pi_0}g(h_0, \Pi_0)}{\left[\dfrac{\partial F(h_0, \Pi_0)}{\partial h_0}\right]^2-\left[g(h_0, \Pi_0)\right]^2}\lambda.\end{aligned}\tag{20}$$

Let us suppose that the variations in the pressure of water vapor in the system, are of two kinds, (1) perceptible, and (2) imperceptible, the latter consisting in very numerous small oscillations. In the time $(t_1 - t_0)$, the perceptible variation is $(\Pi_1 - \Pi_0)$. The relation

$$V = \frac{\Pi_1 - \Pi_0}{t_1 - t_0}$$

we shall call the *velocity of perceptible variation of the pressure of water vapor*. The quantity 2λ indicates the magnitude of the imperceptible variations during the same time. The ratio

$$D = 2\lambda/(t_1 - t_0)$$

is the larger the more imperfectly regulated is the means for producing the perceptible variations of pressure. We shall term it the *coefficient of irregularity*. Finally, the relation

$$v = \frac{h_1 - h_0}{t_1 - t_0}$$

is the *velocity of hydration*. Using this notation, and suppressing the index o, now useless, we find that *the velocity of hydration at the instant* t *is given by the formula*

$$v = \frac{\dfrac{\partial F(h, \Pi)}{\partial \Pi}}{\left[\dfrac{\partial F(h, \Pi)}{\partial h}\right]^2 - \left[g(h, \Pi)\right]^2} \left\{ g(h, \Pi) \frac{|V|}{V} - \frac{\partial F(h, \Pi)}{\partial h} \right\} V$$

$$+ \frac{\dfrac{\partial F(h, \Pi)}{\partial \Pi} g(h, \Pi)}{\left[\dfrac{\partial F(h, \Pi)}{\partial h}\right]^2 - \left[g(h, \Pi)\right]^2} D. \qquad (21)$$

So far we have, for simplicity, limited ourselves to the case in which the temperature is strictly constant. But it is evident that the imperceptible variations of pressure will involve imperceptible variations of temperature, which must, strictly speaking, be taken into account. This is done in the following.

Because of equation (15), the general equation (9) may be written

$$\frac{\partial F(h, \Pi, T)}{\partial h} dh + \frac{\partial F(h, \Pi, T)}{\partial \Pi} d\Pi + \frac{\partial F(h, \Pi, T)}{\partial T} dT + g(h, \Pi, T) |dh| = 0. \qquad (22)$$

Let us consider two consecutive instants, t_0 and t_1. Setting out at the instant t_0 from a pressure Π_0, the pressure Π reaches at the instant t_1 the value Π_1; the degree of hydration passing at the same time from the value h_0 to the value h_1, while the temperature T returns to its initial value T_0.

In the change to which the system has thus been submitted, let us consider, to begin with, an elementary change for which dh is positive. For such a change we shall have

$$\left[\frac{\partial F(h, \Pi, T)}{\partial h} + g(h, \Pi, T)\right] dh + \frac{\partial F(h, \Pi, T)}{\partial \Pi} d\Pi + \frac{\partial F(h, \Pi, T)}{\partial T} dT = 0,$$

an equation which, by neglecting infinitesimals of higher orders, may be given the form

$$\left[\frac{\partial F(h_0, \Pi_0, T_0)}{\partial h_0} + g(h_0, \Pi_0, T_0)\right] dh + \frac{\partial F(h_0, \Pi_0, T_0)}{\partial \Pi_0} d\Pi + \frac{\partial F(h_0, \Pi_0, T_0)}{\partial T_0} dT = 0.$$

Recalling the first inequality (14 bis), we see that in this equation the expression

$$\frac{\partial F(h_0, \Pi_0, T_0)}{\partial \Pi_0} d\Pi + \frac{\partial F(h_0, \Pi_0, T_0)}{\partial T_0} dT$$

is negative.

If, then, we write analogous equations for all elementary changes in which dh is positive, and add them member to member, we get the equation :

$$\left[\frac{\partial F(h_0, \Pi_0, T_0)}{\partial h_0} + g(h_0, \Pi_0 T_0)\right] \sum_{+} dh + \sum_{+} \left[\frac{\partial F(h_0, \Pi_0, T_0)}{\partial \Pi_0} d\Pi + \frac{\partial F(h_0, \Pi_0, T_0)}{\partial T_0} dT\right] = 0. \qquad (23)$$

Similarly, the elementary changes corresponding to negative values of dh give the equation

$$\left[\frac{\partial F(h_0, \Pi_0, T_0)}{\partial h_0} - g(h_0, \Pi_0, T_0)\right] \sum_{-} dh$$
$$+ \sum_{+} \left[\frac{\partial F(h_0, \Pi_0, T_0)}{\partial \Pi_0} d\Pi + \frac{\partial F(h_0, \Pi_0, T_0)}{\partial T_0} dT\right] = 0. \qquad (23 \text{ bis})$$

Multiplying the two members of equation (23) by

$$\frac{\partial F(h_0, \Pi_0, T_0)}{\partial h_0} - g(h_0, \Pi_0, T_0),$$

and the two members of equation (23 bis) by

$$\frac{\partial F(h_0, \Pi_0, T_0)}{\partial h_0} + g(h_0, \Pi_0, T_0),$$

and adding the results obtained, member to member, noting that

$$\sum_{+} dh + \sum_{-} dh = \sum dh = h_1 - h_0$$
$$\sum_{+} d\Pi + \sum_{-} d\Pi = \sum d\Pi = \Pi_1 - \Pi_0,$$
$$\sum_{+} dT + \sum_{-} dT = \sum dT = 0,$$

we find the equation

$$\left\{\left[\frac{\partial F(h_0, \Pi_0, T_0)}{\partial h_0}\right]^2 - \left[g(h_0, \Pi_0, T_0)\right]^2\right\}(h_1 - h_0)$$
$$+ \frac{\partial F(h_0, \Pi_0, T_0)}{\partial h_0} \frac{\partial F(h_0, \Pi_0, T_0)}{\partial \Pi_0} (\Pi_1 - \Pi_0)$$
$$+ g(h_0, \Pi_0, T_0) \sum \left|\frac{\partial F(h_0, \Pi_0, T_0)}{\partial \Pi_0} d\Pi + \frac{\partial F(h_0, \Pi_0, T_0)}{\partial T_0} dT\right| = 0.$$

If we take into account the inequality (13 bis), we may write this in the form

$$\left\{\left[\frac{\partial F(h_0, \Pi_0, T_0)}{\partial h_0}\right]^2 - \left[g(h_0, \Pi_0, T_0)\right]^2\right\}(h_1 - h_0)$$
$$+ \frac{\partial F(h_0, \Pi_0, T_0)}{\partial \Pi_0}\,\frac{\partial F(h_0, \Pi_0, T_0)}{\partial h_0}(\Pi_1 - \Pi_0)$$
$$= g(h_0, \Pi_0, T_0)\frac{\partial F(h_0, \Pi_0, T_0)}{\partial \Pi_0}\sum\left|\,d\Pi + \frac{\dfrac{\partial F(h_0, \Pi_0, T_0)}{\partial T_0}}{\dfrac{\partial F(h_0, \Pi_0, T_0)}{\partial \Pi_0}}\,dT\right|. \qquad (24)$$

Let us set

$$d_1\Pi = d\Pi + \frac{\dfrac{\partial F(h_0, \Pi_0, T_0)}{\partial T_0}}{\dfrac{\partial F(h_0, \Pi_0, T_0)}{\partial \Pi_0}}\,dT. \qquad (25)$$

Since $\Sigma\, dT = 0$, we obtain immediately

$$\sum d_1\Pi = \sum d\Pi = \Pi_1 - \Pi_0\,;$$

hence we may write

$$\sum |d_1\Pi| = |\Pi_1 - \Pi_0| + \mu, \qquad (26)$$

where μ is a quantity which is zero when the variations of Π and T are so regulated that all the quantities $d_1\Pi$ have the same sign, and which in others than this exceptional case is positive.

By means of equations (25) and (26), equation (24) becomes

$$\left\{\left[\frac{\partial F(h_0, \Pi_0, T_0)}{\partial h_0}\right]^2 - \left[g(h_0, \Pi_0, T_0)\right]^2\right\}(h_1 - h_0)$$
$$+ \frac{\partial F(h_0, \Pi_0, T_0)}{\partial \Pi_0}\left\{\frac{\partial F(h_0, \Pi_0, T_0)}{\partial h_0}(\Pi_1 - \Pi_0) - g(h_0, \Pi_0, T_0)\,|\Pi_1 - \Pi_0|\right\}$$
$$= \frac{\partial F(h_0, \Pi_0, T_0)}{\partial \Pi_0}\,g(h_0, \Pi_0, T_0)\mu. \qquad (27)$$

We will now designate by D the *coefficient of irregularity* $\mu/(t_1 - t_0)$; we will also suppress the index o in equation (27) as having become useless, and we find then that the *velocity of hydration at the instant* t *is given by the formula*

$$v = \frac{\dfrac{\partial F(h, \Pi, T)}{\partial \Pi}}{\left[\dfrac{\partial F(h, \Pi, T)}{\partial h}\right]^2 - \left[g(h, \Pi, T)\right]^2} \left\{ g(h, \Pi, T)\frac{|V|}{V} - \frac{\partial F(h, \Pi, T)}{\partial h} \right\} V$$

$$+ \frac{\dfrac{\partial F(h, \Pi, T)}{\partial \Pi} g(h, \Pi, T)}{\left[\dfrac{\partial F(h, \Pi, T)}{\partial h}\right]^2 - \left[g(h, \Pi, T)\right]^2} D. \qquad (21 \text{ bis})$$

3. Discussion of the foregoing formula

Let us examine the consequences of this equation. Suppose, first, that the pressure of water vapor suffers no perceptible variation; then

$$V = 0.$$

The equation (21 bis) is thus reduced to

$$v = \frac{\dfrac{\partial F(h, \Pi, T)}{\partial \Pi} g(h, \Pi, T)}{\left[\dfrac{\partial F(h, \Pi, T)}{\partial h}\right]^2 - \left[g(h, \Pi, T)\right]^2} D. \qquad (28)$$

Taking into account the inequalities (13 bis) and (14 bis), and noting that D is positive, we see that v is opposite in sign to $g(h, \Pi, T)$. If we are studying a *system of the first category*, that is, a *system whose natural states are stable*, v must be positive if the point (Π, h) is above the line of natural states, and negative in the contrary case; hence *below the line of natural states* we must have the inequality

$$g(h, \Pi, T) < 0, \qquad (29)$$

while *above the line of natural states*, we have the inequality

$$g(h, \Pi, T) > 0. \qquad (29 \text{ bis})$$

For the present, we shall draw no further conclusions from equation (28), although it has been of service in other circumstances.[1] The present derivation of it is both more rigorous and more general than the one that I have previously given.

Let us return to equation (21 bis). Analogous equations have been employed in my earlier memoir *On magnetic viscosity*,[2] whose brief derivation of these equations may with advantage be replaced by the foregoing one. Let us consider a point, to take a definite case, situated above the line of natural states, and at this point, the angle a formed by the ascending line and the prolongation of the descending line. The pitch of the ascending line will be

$$\tan a = -\frac{\frac{\partial F(h, \Pi)}{\partial \Pi}}{\frac{\partial F(h, \Pi)}{\partial h} + g(h, \Pi)}; \tag{30}$$

while that of the descending line will be

$$\tan d = -\frac{\frac{\partial F(h, \Pi)}{\partial \Pi}}{\frac{\partial F(h, \Pi)}{\partial h} - g(h, \Pi)}. \tag{30 bis}$$

In the neighborhood of the line of natural states, the quantities

$$\frac{\partial F(h, \Pi)}{\partial \Pi}, \quad \frac{\partial F(h, \Pi)}{\partial h}$$

have finite values. On the contrary, $g(h, \Pi)$ is infinitesimal, $\tan a$ and $\tan d$ have values only infinitesimally different, and the prolongation of the descending line makes an infinitesimal angle a with the ascending line.

Keeping Π constant, let us increase h so that the point (h, Π) departs from the line of natural states. The angle a will at first increase; let us suppose that this angle, continuing to grow, approaches $\pi/2$ as h increases without limit. For this to

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[1] Mém. Acad. Roy. Belg. 56; Mém. Soc. Sci. phys. nat. Bordeaux (5) 4, 452 (1898).

[2] Mém. Soc. Sci. phys. nat Bordeaux (5) 5 (1899).

occur, the ascending line must tend to become parallel to the OΠ axis, while the descending one approaches parallelism with the hO axis; in other words, $\tan a$ must approach zero, and $\tan d$ must increase without limit. And since

$$\frac{\partial F(h, \Pi)}{\partial \Pi}$$

certainly remains finite, for when h increases without limit $v(h, \Pi)$ tends toward the specific volume of pure water, the above conditions are equivalent to this: *When* h *increases without limit,*

$$\frac{\partial F(h, \Pi)}{\partial h} \text{ and } g(h, \Pi)$$

increase without limit by positive values, while

$$\left[\frac{\partial F(h, \Pi)}{\partial h} - g(h, \Pi)\right]$$

tends towards zero through positive values.

Let us take then the equation (21 bis), and write it in the form

$$v = \frac{\dfrac{\partial F(h, \Pi)}{\partial \Pi}}{\left[\dfrac{\partial F(h, \Pi)}{\partial h}\right]^2 - \left[g(h, \Pi)\right]^2} \left\{ g(h, \Pi)(|V| + D) - \frac{\partial F(h, \Pi)}{\partial h} V \right\} \tag{31}$$

The factor before the bracket is always negative, because of the inequalities (13 bis) and (14 bis), and, if h is very large, its absolute value is very large, for the denominator is nearly zero.

The factor between brackets is positive and very large, for

$$\left[\frac{\partial F(h, \Pi)}{\partial h} - g(h, \Pi)\right]$$

being nearly 0, this factor differs little from $g(h, \Pi)D$ when V is positive, and from $g(h, \Pi)(2|V| + D)$ when V is negative.

So, when h *is very large, the velocity of hydration* v *is always negative and very large, whatever be the sign of* V, *the velocity of the perceptible variations of the pressure of water vapor.*

The case is quite different *in the neighborhood of the line of natural states*; for, since $g(h, \Pi)$ is then very small, the equation (31) reduces to

$$v = -\frac{\dfrac{\partial F(h, \Pi)}{\partial \Pi}}{\dfrac{\partial F(h, \Pi)}{\partial h}} V,$$

and *the velocity of hydration* v *always has the same sign as* V, *the velocity of the perceptible variations in the pressure of the water vapor.*

Let us proceed further. We will take the pressure Π and the values of D and $|V|$ as given. There will be a value H of h, larger than the value $h = \eta$ which corresponds to the natural state, for which we have

$$g(H, \Pi)(|V| + D) - \frac{\partial F(H, \Pi)}{\partial H} |V| = 0. \qquad (32)$$

For $h = H$, v will be zero if V is positive, negative if V is negative.

For the values of h which are larger than H, v will be negative whatever may be the sign of V; but the absolute value of v will be larger for negative than for positive values of V. For the values of h lying between H and η, v has always the same sign as V; but the absolute value of v remains larger for negative than for positive values of V.

This absolute value tends to become independent of the sign of V as h approaches η. Let us assume, for instance, that with a velocity V, whose absolute value is supposed invariable, the pressure of water vapor oscillates between the invariable value Π and a value Π', also invariable, and somewhat larger than Π. h starts from an initial value ΠA (Fig. 1), which, let us suppose, is larger than H. The representative point describes at first the segments AA′, A′B, BB′, B′C, CC′, C′D, which descend alternately from left to right and from right to left; but a segment descending from right to left, as B′C, descends more rapidly than the one BB′, descending from left to right and immediately preceding it.

This remains true up to the moment when h becomes equal to or less than H. Suppose, for example, that $\Pi D = H$. Starting from the point D, the representative point will describe a segment DD′ parallel to OΠ; it will then describe the segments D′E, EE′, E′F, FF′ ···, which alternately descend from right to left and ascend from left to right. A descending segment is steeper than the preceding ascending one. The pitches of these

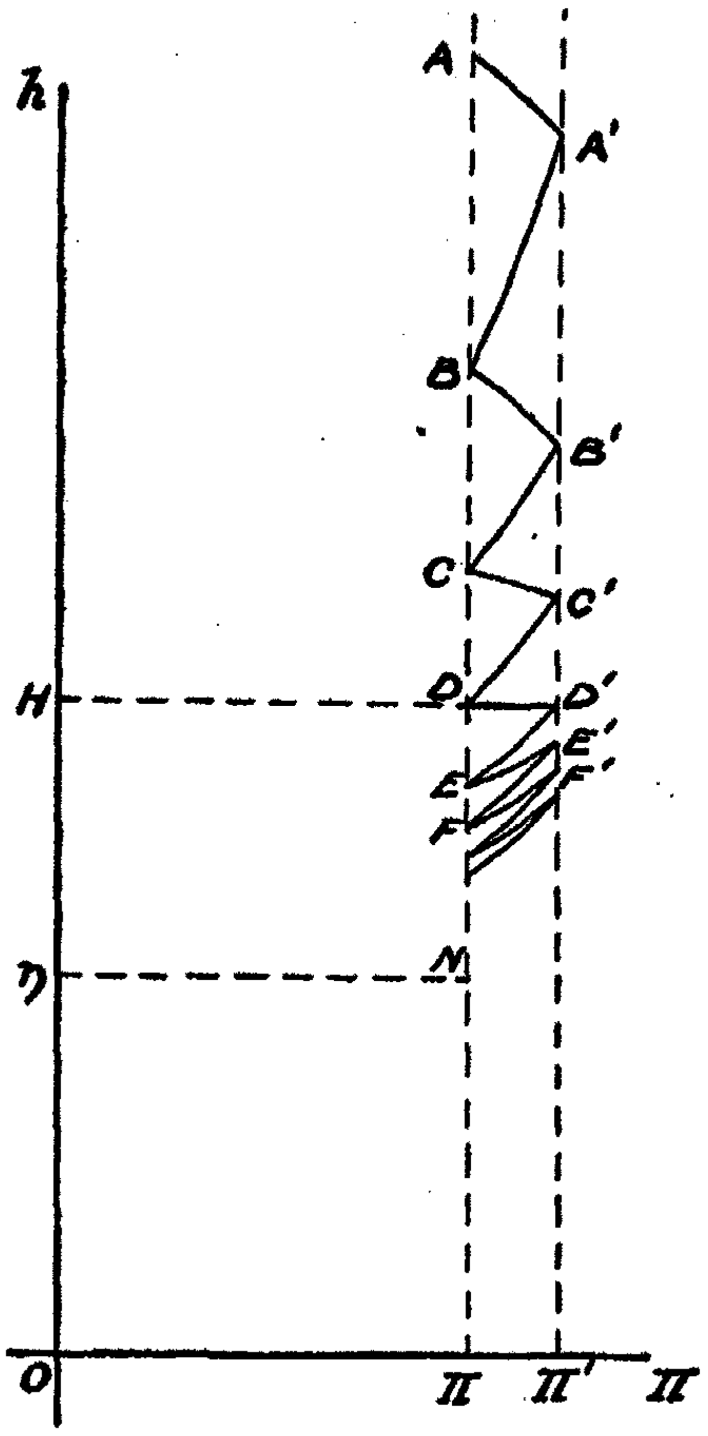

Fig. 1

segments approach each other as we get nearer to N, which represents a natural state.

The value of h which we have designated H, depends upon the pressure Π, but not upon this alone : it depends also upon the ratio $\frac{D}{|V|}$, as is shown by equation (32). If this ratio is very large, equation (32) becomes practically

$$g(H, \Pi) = 0;$$

it shows that the point (Π, H) is none other than the point N, representing the natural state corresponding to the pressure Π. If, on the contrary, $\frac{D}{|V|}$ is very small, then equation (32) becomes

$$g(H, \Pi) - \frac{\partial F(H, \Pi)}{\partial H} = 0,$$

which is satisfied only for $H = +\infty$.

Hence *it is not possible to say that the equation*

$$g(H, \Pi)(|V| + D) - \frac{\partial F(H, \Pi)}{\partial H}|V| = 0 \qquad (32)$$

represents a line on the plane ΠOh, *unless the value of the ratio*

$$\rho = \frac{D}{|V|}$$

is given. As ρ *diminishes from* $+\infty$ *to* 0, *the line in question, setting out from the line of natural states, becomes more and more distant from it and finally reaches infinity in the positive direction of* Oh.

Let us return now to the case in which all the variations in the pressure of water vapor Π are imperceptible. The velocity of hydration v will then be given by the formula

$$v = \frac{\frac{\partial F(h, \Pi, T)}{\partial \Pi} - g(h, \Pi, T)}{\left[\frac{\partial F(h, \Pi, T)}{\partial h}\right]^2 - \left[g(h, \Pi, T)\right]^2} D. \qquad (28)$$

Suppose that we determine, by weighing, the diminution of h during a certain time; it will only be possible to take account of the variations of h above a certain limit ϵ. If Θ is the lapse of time for which the determination is made, then v will be known except as to values of the order of $\frac{\epsilon}{\Theta}$; hence the precision with which v is determined depends upon the lapse of time to which the observation refers, and is proportional to this lapse of time.

Suppose, for instance, that the time Θ is one week; it might happen that the absolute value of v would be lower than $\frac{\epsilon}{\Theta}$. Experimentally, then, this value would not be distinguishable from zero, and the equilibrium would apparently be established. This might not happen if the value for Θ were made one month, whereby the absolute value of v might become larger than $\frac{\epsilon}{\Theta}$, and it would then become evident that the equilibrium apparently existing after one week, was not in reality established.

If, the representative point of the state of the system being in the (Π, h)-plane, the absolute value of the velocity v is less than $\frac{\epsilon}{\Theta}$, *the point* (Π, h) *is said to be within the region of secular variations for the time* Θ *under consideration.* The line separating the region where the absolute value of v is larger than $\frac{\epsilon}{\Theta}$ from the region where it is smaller than $\frac{\epsilon}{\Theta}$ is *the limiting line of secular variations for the time* Θ. This line alters its position for different values of Θ. If Θ increases without limit, then $\frac{\epsilon}{\Theta}$ approaches zero, and the various points on the limiting line will correspond to values of g which approach zero. Therefore, *the limiting line tends to merge in the line of natural states when* Θ *increases without limit; and in general it is the nearer to the line of natural states the greater* Θ *becomes.* In any case, and whatever be the value of Θ, the line of natural states lies in the region of secular variations.

Furthermore, it is quite clear that the limiting line of secular variations for a given period Θ is definite only when the degree of precision ϵ of the method for determining the degree of hydration is given, as also the value D of the coefficient of irregularity of the external actions.

In all my studies relative to tempering and annealing, I have insisted on the role of the region of secular variations.

4. Comparison of the results of the preceding discussion with the observations of van Bemmelen

All the above details have been very carefully noted by van Bemmelen in his various investigations of the dehydration of colloidal jellies. He has given a particularly complete description of the phenomena accompanying the dehydration of colloidal ferric oxide, exposed to the hygrometrically variable air of the laboratory.[1] The following passages are taken from his description:

"From Aug. 2 to Aug. 11 (first period), the water is vaporized with a regular diminishing velocity, and the quantity retained falls from 18.6 to 5.4 H_2O.

"In the second period of 42 days (from the 2d to the 7th week) the loss of water becomes irregular; on nine different days in this period the oxide took up, from the air, more water than it gave off, because of an increased humidity on these days. During this period the water content fell to 4.64 H_2O.

"In the third period, extending from the 7th to the 31st week, every increase in humidity caused an increase in the water content, every decrease a diminution; when the humidity remained constant the water content was invariable. In the first 55 days of this period, a maximum water content of 4.65 H_2O was observed, the hygrometer (of Klinkerfues) marking 86°, and a minimum of 4.58 H_2O, when the hygrometer stood at 69°. The mean of the hygrometer readings was 78°.

"After 55 days, the composition of the jelly was found to be practically the same as before, the sum of the losses in water on 26 of these days (0.24 H_2O) being almost exactly compen-

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[1] Zeit. anorg. Chem. 20, 185 (1899).

sated by the sum of the absorptions on the 27 other days (0.21 H_2O).

"During 19 days following, the minimum water content 4.54 H_2O was observed when the hygrometer marked 70° ; then, in the 35 days following, a maximum of 4.57 H_2O was noted, the hygrometer marking 82°, and a minimum of 4.45 H_2O when the hygrometer marked 65° ; finally, in the following 57 days, the maximum 4.50 H_2O was observed when the hygrometer marked 78°, and the minimum 4.28 H_2O when it stood at 55°. Hence there is still a slight progressive loss in the water content, which is to be attributed, mainly, to the small but repeated variations in the humidity of the air; for when a decrease in humidity has brought about a diminution in the water content, *this does not return to its primitive value* when the humidity increases again."

All the characteristics whose analysis has been rendered possible by the theory will be found noted in the above. First of all, that whatever be the direction of the oscillations of the hygrometer, the water in the colloidal jelly diminishes continually; slowly at first, then more rapidly. Then the direction of the variations of the water content remains no longer constant: the amount of water rises or falls according to the motion of the hygrometer, but the diminutions are much larger than the augmentations. Later on, these two actions in opposite directions compensate one another almost exactly, so that an equilibrium appears to be established; as a matter of fact there is no state of equilibrium, but a *secular diminution* of the water content. This diminution, sensible only after the lapse of a very long time, is due to the accumulation of permanent changes, all in the same direction, resulting from the successive hydrations and dehydrations following the small but repeated risings and fallings of the hygrometer.

Dehydration in an atmosphere of water vapor whose pressure and temperature are kept as nearly constant as possible presents, though in a less degree, the same characteristics as does dehydration in the air of the laboratory. Van Bemmelen indicates this in the following lines:

"At first there is loss of water with decreasing velocity, as I have always observed in the case of combination by absorption. When the daily loss of water has fallen to a low value, it begins to decrease irregularly, becoming sometimes constant, sometimes zero, or again changing to a gain. Finally, at the end of several months, the water content becomes approximately constant. ..."

For each pressure Π of water vapor, van Bemmelen marks a point *a* (Fig. 2) whose ordinate OH = H represents the value of *h* below which the direction of the variation becomes variable. Below this point, he marks the points ½, 1, 2, 3, 4, 5, 6, representing values of *h* observed one-half month, one month, two, three, four, five, and six months later. These points, situated one below the other, approach nearer and nearer to one another. Van Bemmelen has traced the locus of the point *a*, calling it the curve A, and the locus of the point 6, which he calls the curve A_1, or the *curve of approximate equilibria.* In the notation I

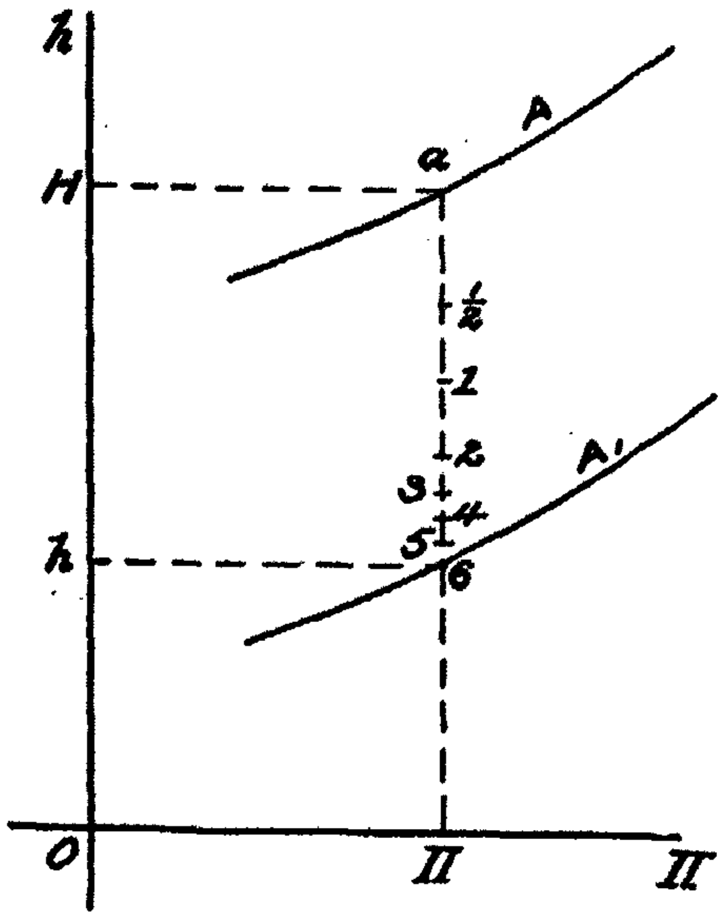

Fig. 2

have used, the curve A_r is *the limiting line of secular variations* for periods of the order of a month; these lines A and A_r rise from left to right. These lines become definite only on the supposition that the quantities D and $|V|$ vary but little from one experiment to another.

Van Bemmelen had made similar observations in his earlier investigation of the dehydration of gelatinous silica.[1] In the plane ΠOh, he draws a curve which he calls A_β, defining it as follows: "The points of this curve represent the composition of the jelly when equilibrium is approximately established; I mean by that, that the loss of water for several days is so small that it amounts to less than 0.1 H_2O per week, and then becomes gradually so small that only after months does it attain the value 0.3 to 0.5 H_2O."

The line thus defined is plainly that which I have named *the limiting line of secular variations* for the degree of precision $\epsilon = 0.1$ H_2O and the period $\Theta =$ one week.

This approximate equilibrium is followed by a period of secular diminution in the water content. "Experiment shows that, after this approximate equilibrium is established, there is still a loss of water, which becomes slower with the time. In those experiments where dehydration was made as rapid as possible, the rapidity of this loss decreases regularly during the first four months; where the dehydration was made as slow as possible, this regular diminution lasts through the first eight months. In the following months the loss, which is very slight, becomes more irregular. ··· Three observations were carried on over a period of from two to three years, under the increased pressures of 12.2 mm, 11.6 mm, and 10.6 mm. In the last year the loss of water was very small, or zero. One may say, therefore, that, without altogether ceasing, the dehydration becomes, after two years, extraordinarily slow."

5. Phenomena of hydration and dehydration in the region of secular variations

If we take a system in a state represented by a point on the limiting line of secular variations, and first increase, then de-

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[1] Zeit. anorg. Chem. 13 (1896); particularly pp. 241, 250, 280.

crease the pressure of aqueous vapor, we shall notice certain phenomena, whose laws have been stated by van Bemmelen. We can explain these laws by means of considerations very similar to those which have served us in studying the properties of the irreversible nickel steels of Guillaume.[1]

Let us suppose that the representative point for the state of the system lies on the line bounding the region of secular variations for the conditions of irregularity experimentally realized, and for a given period of observation, — say, for example, one week. Let us vary the pressure in such a way that the point comes into the region of secular variations; then, let us keep this pressure practically fixed, so that its variations are reduced to the imperceptible variations upon which the coefficient D depends.

From the definition of the region of secular variations, if we observe for only one week, we shall find no appreciable change in the degree of hydration, and hence no appreciable displacement of the point. In order to observe such a displacement, it would be necessary to increase very much the time of the observations. Hence this first proposition:

If, *by perceptible changes in the pressure of water vapor, the representative point is displaced into the region of secular variations, then after each change the approximate equilibrium will be found to be immediately established.*

According to equation (28), and the definition of the region of secular variations, the absolute value of the expression

$$\frac{\frac{\partial F(h, \Pi)}{\partial \Pi} g(h, \Pi)}{\left[\frac{\partial F(h, \Pi)}{\partial h}\right]^2 - \left[g(h, \Pi)\right]^2} D$$

will be, for every point in that region, less than $\frac{\epsilon}{\Theta}$, a ratio whose numerator ϵ is very small, while its denominator Θ is very large. Even supposing D to be small, we conclude that for every point in the region of secular variations the absolute value

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[1] Mém. Soc. Sci. phys. nat. Bordeaux (5), 4, 452 (1898).

of $g(h, \Pi)$ is very small, and negligible in comparison with that of

$$\frac{\partial F(h, \Pi)}{\partial h}.$$

Hence for every change where the path of the representative point does not leave the region of secular variations, the formula (21 bis) reduces practically to

$$v = -\frac{\dfrac{\partial F(h, \Pi)}{\partial \Pi}}{\dfrac{\partial F(h, \Pi)}{\partial h}} V. \qquad (33)$$

It is plain then that if the velocity V of the perceptible variations in the pressure of water vapor changes its sign without changing its absolute value, the velocity of hydration will change in essentially the same way. This may be stated in the form: *Every change in which the representative point remains within the region of secular variations is practically reversible.*

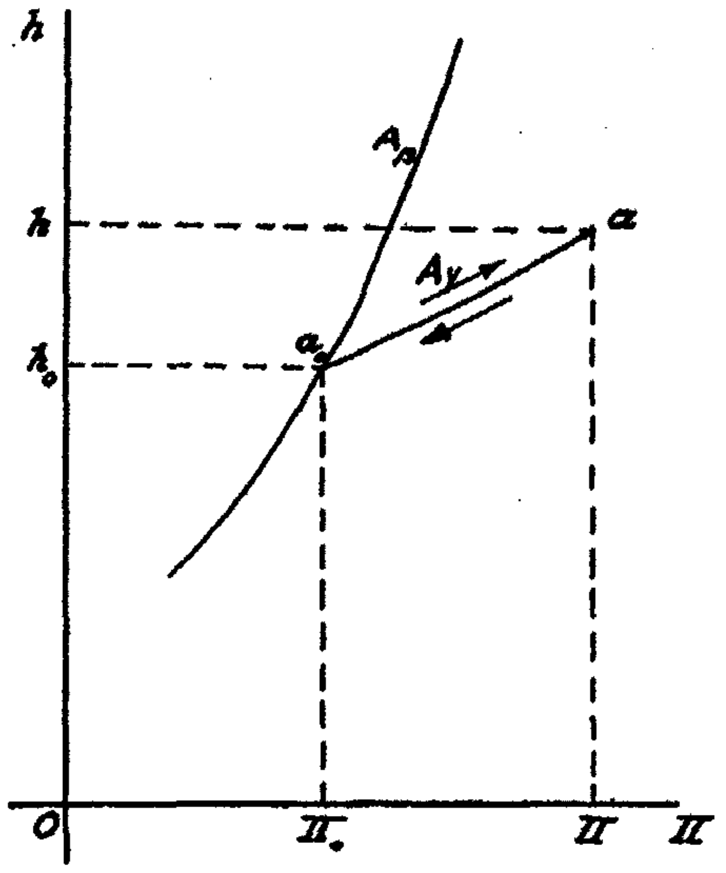

Fig. 3

Let us imagine, for example (Fig. 3), a point a_0 (Π_0, h_0) taken on van Bemmelen's line A_β which limits the region of secular variations. Let us increase the pressure of water vapor from Π_0 to Π; the representative point will describe a path a_0a, which brings it to the point $a(\Pi, h)$. Now let us restore the pressure of water vapor to the value Π_0; the representative point will return practically to a_0, following essentially the path aa_0. This path, A_γ of van Bemmelen, represents a practically reversible change. Van Bemmelen has more than once very clearly pointed out the characteristics of these nearly reversible lines.[1]

CHAPTER II.

PHENOMENA OBSERVED WHEN DEHYDRATION HAS REACHED AN ADVANCED STAGE

1. Formulation of the problem of the absorption of water vapor by a colloidal substance, when this is accompanied by another change of state also affected by hysteresis

The phenomena to which the above analysis applies are those observed upon beginning to dehydrate a substance like gelatinous silica. After the operation has been carried to a certain point, new phenomena appear; these are described by van Bemmelen[2] as follows:

"Let us suppose the dehydration brought about in such a way that approximate equilibrium has time to become established at each new pressure. When the water content lies between the values 3 and 1, 5 H_2O, the pressure of water vapor being between 10 and 4.5 mm, there is produced in the jelly a visible change which I have called "turning" (*Umschlag*) ···. The jelly first becomes dim at some point, then opalescent with a blue fluorescence, then white with a porcelain-like sheen, and finally reaches an opaque, wan, chalky whiteness.

"This clouding commences in one or in several points, and spreads thence throughout the mass."

"... If the dehydration is continued, the cloudiness dis-

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[1] Zeit. anorg. Chem. 13, 252 (1896); 18, 103 (1898); 20, 191 (1899).

[2] Ibid. 13, 245 (1896).

appears and its disappearance is accompanied by phenomena similar to those which marked its development: the jelly assumes first the aspect of porcelain, then the blue fluorescency, and then assumes gradually the homogeneity and transparency of glass, which is retained throughout all further dehydration.

"In the same way, if the jelly is submitted to a higher pressure of water vapor immediately after it has turned, it absorbs water and becomes homogeneous and transparent, like glass.

"All these transformations can be produced in the reverse directions."

The hydration and dehydration accompanying the phenomena just described are subject to very marked hysteresis, and it is this which we shall study in the present chapter.

Van Bemmelen[1] is disposed to assign a heterogeneous structure to hydrated silica which manifests these various phenomena, being led to this conclusion by the analogy of certain phenomena observed by microscopists for hydrated jellies of organic or even of mineral origin. He regards it as composed of a colloidal hydrate in very thin lamellæ, forming the walls of an extremely fine cellular net-work whose cavities are filled with another, liquid, hydrate.

Without discussing this hypothesis here, we will retain one essential idea contained in it; namely, that *the water content alone does not suffice to characterize the state of a hydrated gelatinous silica.* Some other datum is necessary; for instance, adopting the hypothesis of van Bemmelen, we must know also the ratio between the mass of colloidal hydrate and the mass of the liquid hydrate.

We shall agree then that in order to define the state of a hydrated colloid, it is necessary to add to the temperature T *and the specific volume* v, *two other normal variables, one of which is the degree of hydration* h, *and the other a certain variable* x, *whose variations mark a change of state concerning which we shall make no hypothesis.*

Let us assume at the outset that the system is not affected

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[1] Zeit. anorg. Chem. 18, 14 (1898).

by hysteresis, and let us study the conditions of equilibrium according to the method employed in Chapter I., § 1, retaining the notation there used. A virtual isothermal change involves an uncompensated work for which the expression, by analogy with (1), will be

$$\begin{aligned} d\tau = & - m(1+h)\left(\frac{\partial \mathfrak{F}}{\partial v} + \Pi\right)dv \\ & - M\left(\frac{\partial \mathfrak{G}}{\partial V} + \Pi\right)dV \\ & - m\left[\mathfrak{F} + \Pi v + (1+h)\frac{\partial \mathfrak{F}}{\partial h} - \mathfrak{G} - \Pi V\right]dh \\ & - m(1+h)\frac{\partial \mathfrak{F}}{\partial x}dx. \end{aligned}$$

Equating this expression to zero, we find the conditions of equilibrium

$$\left.\begin{aligned} \frac{\partial \mathfrak{F}(v, h, x, T)}{\partial v} &= -\Pi, \\ \frac{\partial \mathfrak{G}(V, T)}{\partial V} &= -\Pi, \end{aligned}\right\} \qquad (34)$$

$$\left.\begin{aligned} \mathfrak{F}(v, h, x, T) + \Pi v + (1+h)\,\frac{\partial \mathfrak{F}(v,h,x,T)}{\partial h} & \\ - \mathfrak{G}(V, T) - \Pi V &= 0, \\ \frac{\partial \mathfrak{F}(v, h, x, T)}{\partial x} &= 0. \end{aligned}\right\} \qquad (35)$$

Let us admit, now, that the variables v *and* V *are free from hysteresis, and that the variables* h *and* x, *playing the role of privileged variables, are affected by hysteresis.* This hypothesis signifies that the conditions of equilibrium (34) are retained, but that the conditions (35) are replaced by the conditions

$$\left.\begin{aligned}
&\left[\frac{\partial\mathfrak{F}(v,h,x,\mathrm{T})}{\partial v}+(1+h)\frac{\partial^2\mathfrak{F}(v,h,x,\mathrm{T})}{\partial h\partial v}+\Pi\right]dv\\
&\qquad\qquad-\left[\frac{\partial\mathfrak{G}(\mathrm{V},\mathrm{T})}{\partial\mathrm{V}}+\Pi\right]d\mathrm{V}\\
&+\left[2\frac{\partial\mathfrak{F}(v,h,x,\mathrm{T})}{\partial h}+(1+h)\frac{\partial^2\mathfrak{F}(v,h,x,\mathrm{T})}{\partial h^2}\right]dh\\
&+\left[\frac{\partial\mathfrak{F}(v,h,x,\mathrm{T})}{\partial x}+(1+h)\frac{\partial^2\mathfrak{F}(v,h,x,\mathrm{T})}{\partial h\partial x}\right]dx\\
&+\left[\frac{\partial\mathfrak{F}(v,h,x,\mathrm{T})}{\partial\mathrm{T}}+(1+h)\frac{\partial^2\mathfrak{F}(v,h,x,\mathrm{T})}{\partial h\partial\mathrm{T}}-\frac{\partial\mathfrak{G}(\mathrm{V},\mathrm{T})}{\partial\mathrm{T}}\right]d\mathrm{T}\\
&\qquad\qquad+f_h(v,\mathrm{V},h,x,\mathrm{T},\Pi)\,|dh|=0,\\
&\frac{\partial^2\mathfrak{F}(v,h,x,\mathrm{T})}{\partial v\partial x}dv+\frac{\partial^2\mathfrak{F}(v,h,x,\mathrm{T})}{\partial h\partial x}dh+\frac{\partial^2\mathfrak{F}(v,h,x,\mathrm{T})}{dx^2}dx\\
&\qquad+\frac{\partial^2\mathfrak{F}(v,h,x,\mathrm{T})}{\partial x\partial\mathrm{T}}d\mathrm{T}+f_x(v,\mathrm{V},h,x,\mathrm{T},\Pi)\,|dx|=0.
\end{aligned}\right\}\quad(36)$$

Solving equations (34) for v and V, we find

$$\left.\begin{aligned}
v&=v(h,x,\mathrm{T},\Pi),\\
\mathrm{V}&=\mathrm{V}(\mathrm{T},\Pi).
\end{aligned}\right\}\quad(37)$$

Then let us set

$$\left.\begin{aligned}
&\mathfrak{F}[v(h,x,\mathrm{T},\Pi),h,x,\mathrm{T}]+\Pi v(h,x,\mathrm{T},\Pi)=\phi(h,x,\mathrm{T},\Pi),\\
&\mathfrak{G}[\mathrm{V}(\mathrm{T},\Pi),\mathrm{T}]+\Pi\mathrm{V}(\mathrm{T},\Pi)=\Phi(\mathrm{T},\Pi),\\
&f_h[v(h,x,\mathrm{T},\Pi),\mathrm{V}(\mathrm{T},\Pi),h,x,\mathrm{T},\Pi]=g_h(h,x,\mathrm{T},\Pi),\\
&f_x[v(h,x,\mathrm{T},\Pi),\mathrm{V}(\mathrm{T},\Pi),h,x,\mathrm{T},\Pi]=g_x(h,x,\mathrm{T},\Pi),
\end{aligned}\right\}\quad(38)$$

and it is easily seen, by reasoning as in Chapter I., § 1, that the conditions (34) and (36) may be replaced by the conditions (37) and

$$\frac{\partial^2}{\partial h\partial\Pi}\Big[(1+h)\phi(h,x,\mathrm{T},\Pi)-h\Phi(\mathrm{T},\Pi)\Big]d\Pi,$$

$$+\frac{\partial^2}{\partial h\partial\mathrm{T}}\Big[(1+h)\phi(h,x,\mathrm{T},\Pi)-h\Phi(\mathrm{T},\Pi)\Big]d\mathrm{T}$$

$$+ \frac{\partial^2}{\partial h^2}\Big[(1+h)\phi(h, x, \mathrm{T}, \Pi)\Big]dh$$

$$+ \frac{\partial^2}{\partial h \partial x}\Big[(1+h)\phi(h, x, \mathrm{T}, \Pi)\Big]dx + g_h(h, x, \mathrm{T}, \Pi)\,|dh| = 0, \quad (39)$$

$$\frac{\partial^2\phi(h, x, \mathrm{T}, \Pi)}{\partial \Pi \partial x}d\Pi + \frac{\partial^2\phi(h, x, \mathrm{T}, \Pi)}{\partial \mathrm{T} \partial x}d\mathrm{T}$$

$$+ \frac{\partial^2\phi(h, x, \mathrm{T}, \Pi)}{\partial h \partial x}dh + \frac{\partial^2\phi(h, x, \mathrm{T}, \Pi)}{\partial x^2}dx$$

$$+ g_x(h, x, \mathrm{T}, \Pi)\,|dx| = 0. \quad (40)$$

Such are the conditions which we should have to submit to a general treatment. But a circumstance simplifies this discussion. The phenomena here to be studied are all explained by supposing that $g_h(h, x, \mathrm{T}, \Pi)$ *retains a very small value* while they are produced. Noting then that equation (39) may be written

$$d\Big[\phi(h, x, \mathrm{T}, \Pi) + (1+h)\frac{\partial\phi(h, x, \mathrm{T}, \Pi)}{\partial h} - \Phi(\mathrm{T}, \Pi)\Big]$$

$$+ g_h(h, x, \mathrm{T}, \Pi)\,|dh| = 0,$$

or, because of equation (15),

$$d\mathrm{F}(h, x, \mathrm{T}, \Pi) + g_h(h, x, \mathrm{T}, \Pi)\,|dh| = 0, \quad (41)$$

we see that the function $\mathrm{F}(h, x, \mathrm{T}, \Pi)$ remains practically constant throughout a change, provided this change does not give a very large value to the sum $\Sigma|dh|$.

Then throughout the course of a series of changes which are not sufficiently extended to give to $\Sigma|dh|$ a very large value, of the order of $\frac{1}{g_h(h, x, \mathrm{T}, \Pi)}$, the equation (41) may be replaced by the equation

$$\mathrm{F}(h, x, \mathrm{T}, \Pi) = \mathrm{C}, \quad (42)$$

where C retains a constant value. If it is desired to follow out a change of such extent that $\Sigma|dh|$ has a value comparable with $\frac{1}{g_h(h, x, \mathrm{T}, \Pi)}$, it will be necessary to divide the change into a large number of successive changes, and apply equation (42) to each of these, choosing, however, for each one, a different value of the constant C.

Solving equation (42) for h, we find

$$h = \mathfrak{h}(x, \mathrm{T}, \Pi, \mathrm{C}). \tag{43}$$

Putting

$$\left.\begin{aligned} \phi[\mathfrak{h}(x, \mathrm{T}, \Pi, \mathrm{C}), x, \mathrm{T}, \Pi] &= \psi(x, \mathrm{T}, \Pi, \mathrm{C}), \\ g_x[\mathfrak{h}(x, \mathrm{T}, \Pi, \mathrm{C}), x, \mathrm{T}, \Pi] &= \gamma_x(x, \mathrm{T}, \Pi, \mathrm{C}), \end{aligned}\right\} \tag{44}$$

the relation (40) will plainly become

$$\frac{\partial^2\psi(x, \mathrm{T}, \Pi, \mathrm{C})}{\partial x^2}dx + \frac{\partial^2\psi(x, \mathrm{T}, \Pi, \mathrm{C})}{\partial x \partial \mathrm{T}}d\mathrm{T}$$

$$+ \frac{\partial^2\psi(x, \mathrm{T}, \Pi, \mathrm{C})}{\partial x \partial \Pi}d\Pi + \gamma_x(x, \mathrm{T}, \Pi, \mathrm{C})|dx| = 0. \tag{45}$$

In place of saying that a realizable change of the system is governed by the conditions (40) and (42), we may say that such a change is governed by conditions (43) and (45).

Now, for each particular value of C, the condition (45) has precisely the form which applies to realizable changes of a system defined by one variable affected by hysteresis. This condition may be discussed by familiar methods.

In particular, if T is kept constant, it furnishes us with a family of ascending and a family of descending lines in the plane $\Pi O x$, to which a line of natural states should be added. For each one of these lines drawn in the plane $\Pi O x$, equation (43) gives a corresponding line in the plane $\Pi O h$. We shall not enter here into the detailed study of this double mode of representation, as has been done elsewhere;[1] it will suffice to recall certain propositions regarding the representation in the plane $\Pi O h$, the only one which at present interests us.

The ascending as well as the descending lines in the plane $\Pi O h$ must satisfy the law of the displacement of equilibrium by changes of pressure. The same applies to the line of natural

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[1] To appear in Zeit. phys. Chem.

states, at least if they are stable. And, finally, every realizable closed cycle satisfies the axiom of Clausius.

The volume of the system has the value

$$u = \mathrm{M}\mathrm{V}(\Pi, \mathrm{T}) + m(1 + h)v(h, x, \Pi, \mathrm{T}). \tag{46}$$

Its increase, in any change, is

$$\begin{aligned} du = {} & \mathrm{V}(\Pi, \mathrm{T})d\mathrm{M} + \mathrm{M}\left(\frac{\partial \mathrm{V}}{\partial \Pi}d\Pi + \frac{\partial \mathrm{V}}{\partial \mathrm{T}}d\mathrm{T}\right) \\ & + m\left[v + (1 + h)\frac{\partial v}{\partial h}\right]dh \\ & + m(1 + h)\left(\frac{\partial v}{\partial x}dx + \frac{\partial v}{\partial \Pi}d\Pi + \frac{\partial v}{\partial \mathrm{T}}d\mathrm{T}\right). \end{aligned}$$

But we have

$$d\mathrm{M} = -m\,dh\,;$$

and, observing that v is very small with respect to V, we find that we have essentially

$$du = -m\mathrm{V}(\Pi, \mathrm{T})dh + \mathrm{M}\left(\frac{\partial \mathrm{V}}{\partial \Pi}d\Pi + \frac{\partial \mathrm{V}}{\partial \mathrm{T}}d\mathrm{T}\right).$$

In particular, in a virtual change, accomplished without variation of temperature or pressure, this approximate equation becomes

$$du = -m\mathrm{V}(\Pi, \mathrm{T})dh. \tag{47}$$

In this case, the increase in the volume of the system has the contrary sign to the increase in the degree of hydration.

Now, the law for the displacement of equilibrium by change of pressure runs thus:

A variation of pressure at constant temperature produces in the system a certain change in the values of h and x; if this change were produced virtually, without change either of pressure or temperature, it would be accompanied by a change of volume having a contrary sign to the original variation of pressure. This, then, taken together with the preceding, shows that the variation of h will be of the same sign as the change of pressure.

By applying this last statement successively to the ascending and descending lines and to the line of natural states, we obtain the following theorems:

In the plane ΠOh, *the ascending lines rise from left to right; the descending fall from right to left; the line of natural states rises from left to right.*

Every realizable closed cycle must satisfy the inequality of Clausius. For an isothermal cycle, this inequality asserts that the external work accomplished during the cycle is positive. In the case in point, this inequality reduces to

$$\int \Pi du < 0.$$

But an integration by parts gives

$$\int \Pi du = \int d(\Pi u) - \int u\, d\Pi\ ;$$

and since, for a closed cycle,

$$\int d(u\Pi) = 0,$$

our inequality reduces to

$$\int u\, d\Pi > 0. \tag{48}$$

The u is given by equation (46), which, because of the smallness of v as against V, reduces to

$$u = \mathrm{MV}(\Pi, \mathrm{T}).$$

T is here constant. On the other hand, if we denote by $\mathfrak{M}$ the total mass of water contained in the system, whether in the state of vapor or as water absorbed by the colloid, we have

$$\mathfrak{M} = \mathrm{M} + mh.$$

We have therefore, practically,

$$\int u\, d\Pi = \mathfrak{M} \int \mathrm{V}(\Pi) d\Pi - m \int h \mathrm{V}(\Pi) d\Pi.$$

Now, for a closed cycle,

$$\int \mathrm{V}(\Pi) d\Pi = 0;$$

and, m being essentially positive, the inequality (48) reduces to

$$\int h\mathrm{V}(\Pi)d\Pi < 0. \tag{49}$$

The closed cycle under consideration is represented in the plane $\Pi O h$ by a closed line. If this line runs clockwise, we have

$$\int h\mathrm{V}(\Pi)d\Pi = \int\int \mathrm{V}(\Pi)d\Pi dh,$$

the double integral extending over all the elements $d\Pi.dh$ of the area surrounded by the closed line; if the line runs counterclockwise, we have

$$\int h\mathrm{V}(\Pi)d\Pi = -\int\int \mathrm{V}(\Pi)d\Pi dh.$$

Inequality (49) thus gives the following theorem:

In the plane ΠOh *every realizable isothermal cycle is represented by a closed counterclockwise line.*

2. Comparison of the results of the preceding theory with the experimental facts

Do the propositions just deduced accord with the observations of van Bemmelen on the dehydration of gelatinous silica and of colloidal ferric oxide[1]? We will content ourselves with a comparison with the earlier observations, since they are the more extended and the later ones are analogous with them.

Let us dehydrate a gelatinous silica, giving time after each variation of the pressure of water vapor for the approximate equilibrium to become established. The representative point describes the curve which we have called the limiting line of the region of secular variations, called by van Bemmelen the line A_β.

Dehydration being well advanced, and the representative point being at O (Fig. 4), the 'turning' takes place. If we continue to decrease the pressure of water vapor, we follow a first descending line, OA, called by van Bemmelen the line A_a. This line descends from right to left, at first very rapidly, then

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[1] Zeit. anorg. Chem. 13, 233 (1896); Ibid. 20, 185 (1899).

more slowly. When the pressure falls to zero, the silica still retains a certain quantity of water, so that the descending line OA cuts the O*h* axis in a point A whose ordinate is positive.

Let us now increase the pressure of water vapor from zero

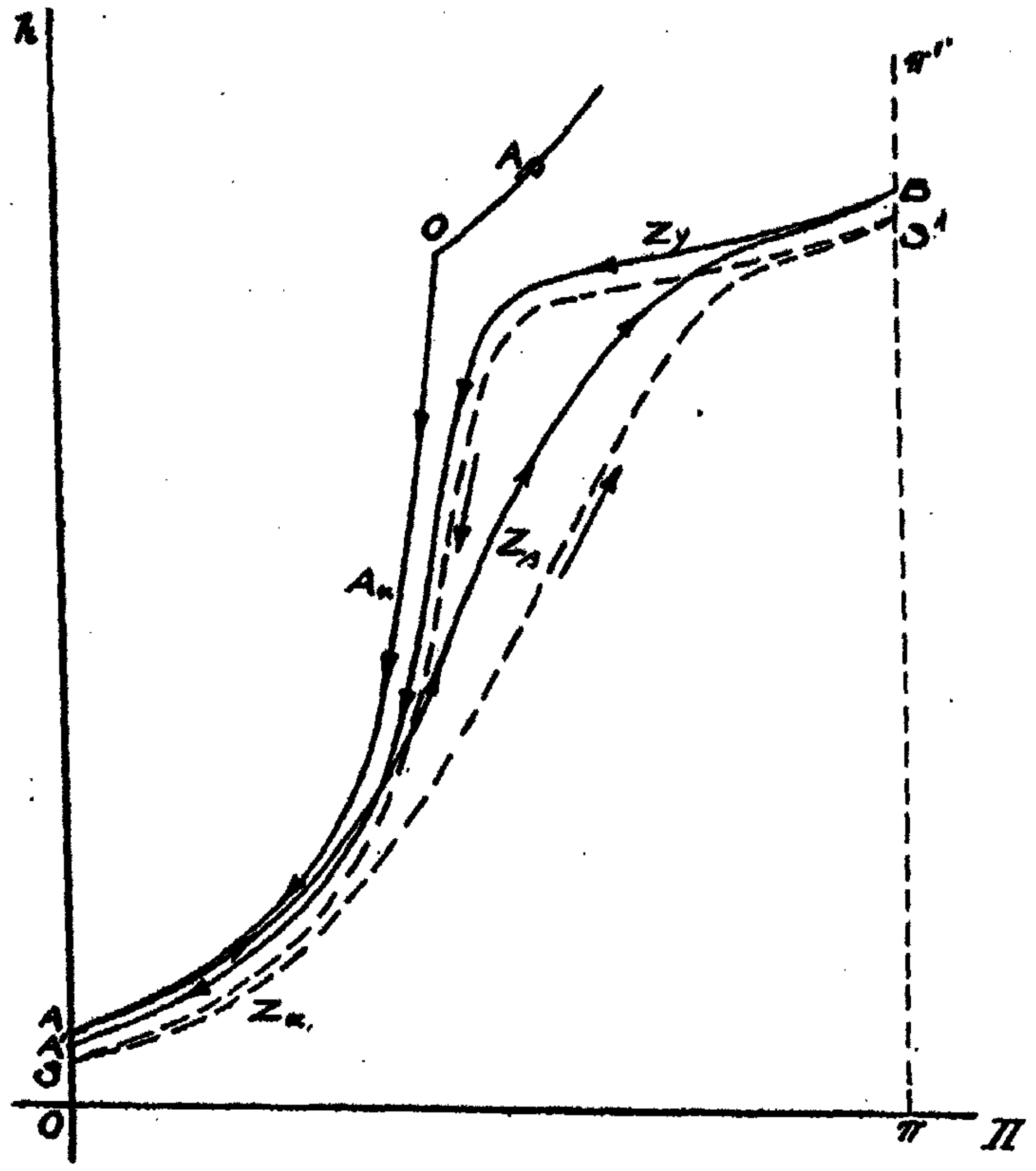

Fig. 4

to π, (Π = 12.7 mm), the pressure of saturated vapor at 15°, at which temperature van Bemmelen's observations were made. We follow thus an ascending line AB rising from left to right. At first, throughout an arc called by van Bemmelen Z_a this ascending line is almost coincident with the descending line OA. Later on, it goes off from that line to the right, forming an arc

Z_β, which rises at first rapidly, then more slowly, and at last, in the part Z_γ, very slowly, and ends at the point B.

Let us now, for the second time, decrease the pressure of water vapor from π, ($\Pi = 12.7$ mm), to zero. We follow then the descending line BA′. This is at first scarcely distinguishable from that part of the ascending line AB which van Bemmelen calls Z_γ. It then continues to descend slowly, nearly to the point O, forming a branch which van Bemmelen also designates Z_γ; it then commences to fall rapidly, remaining very near the first descending line OA or A_α; and it meets the line O*h* in a point A′, a little below A. In a repetition of these operations, the representative point would tend to describe the closed cycle SS′ marked by dotted lines in Fig. 4.

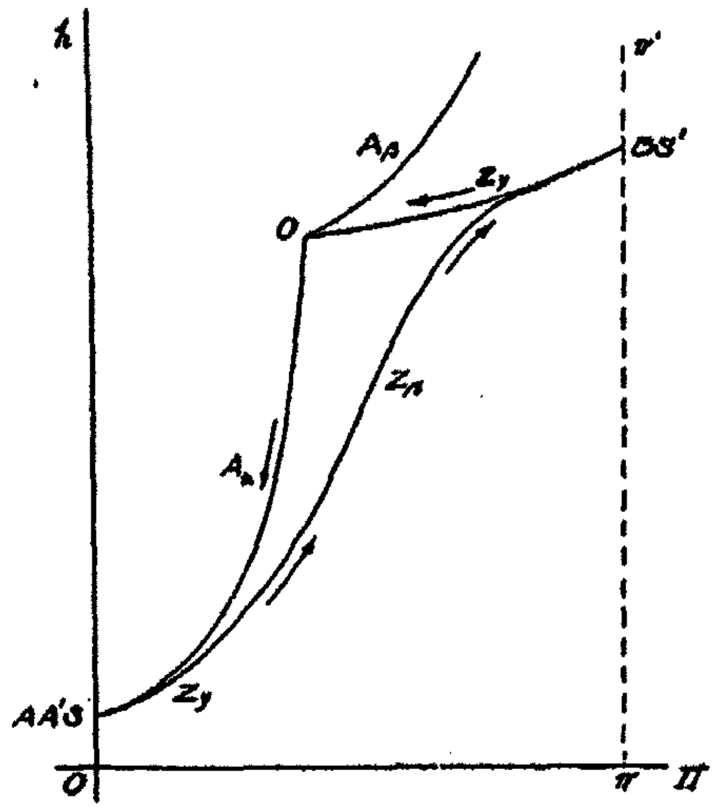

Fig. 5

It is possible thus to interpret the observations of van Bemmelen in conformity with the general theory of hysteresis. Van Bemmelen has given a different interpretation, by regarding as rigorously coincident those points and lines which, in the above, have been regarded merely as very near one another. The scheme presented in Fig. 4 is thus replaced by the one in Fig. 5.

But it is clear, since the observations have only a restricted degree of accuracy, that the first scheme represents the facts quite as well as the second, from which it differs by an amount which

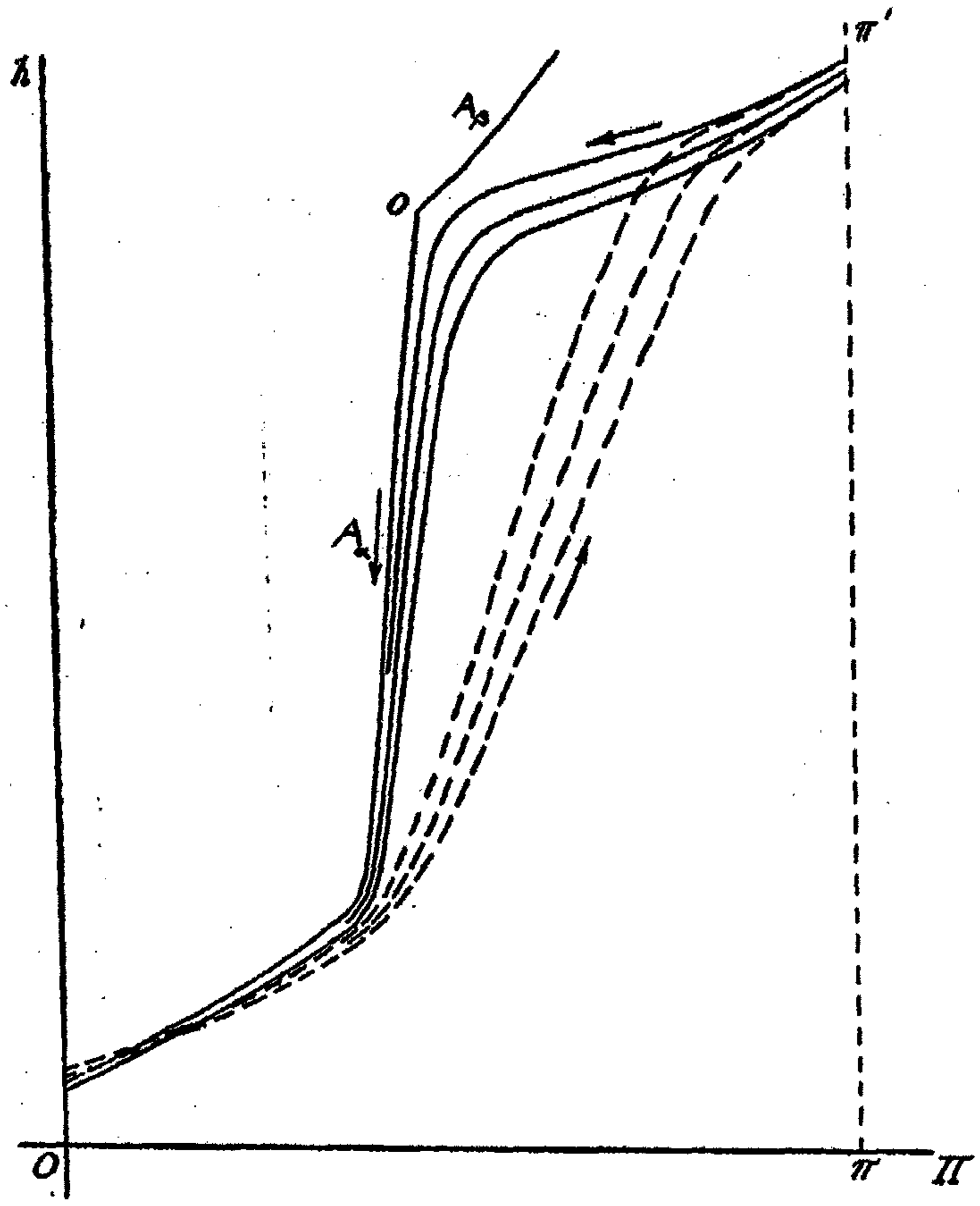

Fig. 6

may be made as small as desired. It will even be observed that the representation in Fig. 4 agrees better with the figures representing van Bemmelen's observations, than does his own scheme, Fig. 5.

Fig. 6 gives, in conformity with the preceding theory, a sheaf of ascending curves marked in dotted lines, and of descending curves in solid lines. If care be taken to avoid confusing those lines which lie so near together as to be indistinguishable by experiment, this scheme will be found to agree very well with the observations of van Bemmelen on what he calls the *intermediate curves.*

Do the observations of van Bemmelen give us any information regarding the line of natural states? If a hydrated gelatinous silica be maintained for a long time at practically constant temperature and pressure of aqueous vapor, this silica changes in a manner which tends towards the natural state for the given temperature and pressure. If, at the same temperature and pressure of aqueous vapor, two hydrated jellies undergo change, one becoming more hydrated, the other dehydrated, so that they tend towards the same limiting state, then this latter is certainly a natural state.

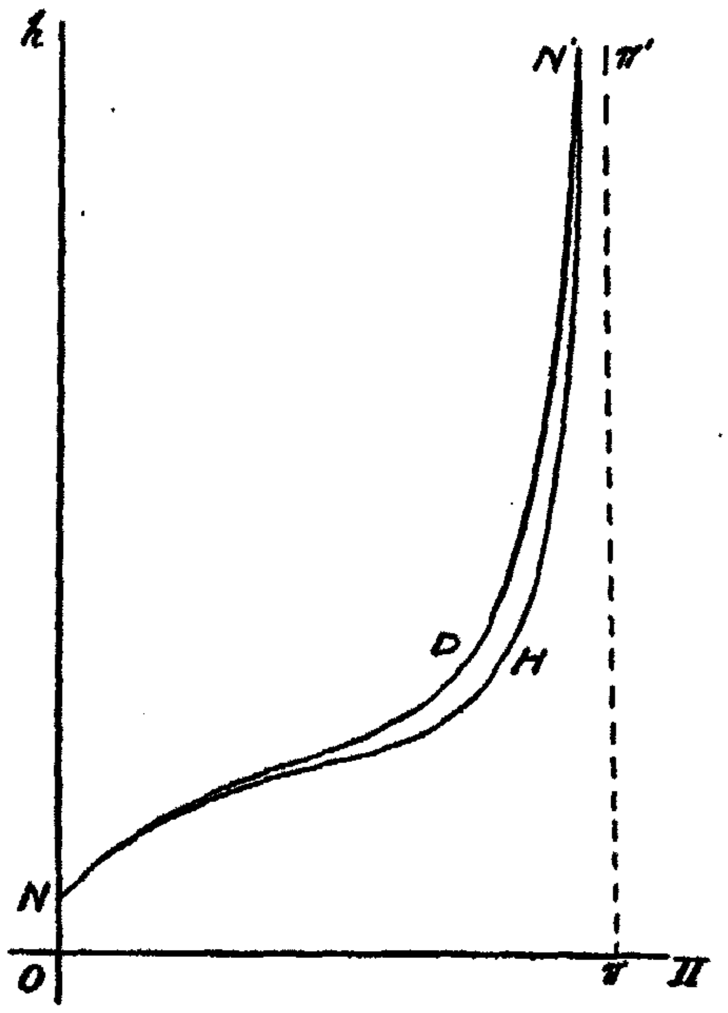

Fig. 7

Van Bemmelen[1] has made experiments of this kind, at a temperature of 15°, under various pressures. Sometimes the two jellies, one of which gives up and the other takes in water, arrive, after a more or less extended period of time, at the same limiting state; at other times, even after the lapse of years, the two jellies still display a noticeable difference in composition, this difference diminishing so slowly that its change in one or two years is imperceptible. The limiting representative points for dehydration lie on a curve NDN′ (Fig. 7); those for hydration on another curve NHN′. Near the ends N, N′, the two curves coalesce; but in their middle parts they are separated by an appreciable interval; instead of forming a single line, which would be the line of natural states, they form a very narrow cycle. It would, no doubt, require observations over many years to observe the coalescence of the two sides of this cycle in a double line.

3. Influence of secular variations of h on the preceding phenomena

All the above developments are on the supposition that the quantity designated by C is invariable; that is to say, not only does the function $g_h(h, x, \mathrm{T}, \Pi)$ remain very small, but, likewise, the sum $\Sigma|dh|$, throughout the changes studied, remains very small with respect to $\frac{1}{g_h(h, x, \Pi, \mathrm{T})}$. If both of these conditions are not fulfilled, C cannot be treated as a constant, and the preceding developments are no longer exact. We shall see what changes will have to be made in them.

Let us suppose that two identical jellies have been brought, at a pressure Π_0 and a temperature T_0, into the same state, h_0, x_0, which, let us say, is a state of approximate equilibrium. Let us suppose this state to be near the one where 'turning' manifests itself. If, at this moment, we calculate the value of the quantity C for each of them, we shall find the same value, c, for both.

Let us take the first of these jellies, and, setting out from the state which has just been reached, let us submit it to a series

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[1] Zeit. anorg. Chem. 13, 271; and Fig. 17, 354 (1896).

of changes during which the sum $\Sigma|dh|$ remains negligible with respect to the very large quantity $\frac{1}{g_h(h, x, T, \Pi)}$. During these changes the quantity C may be considered to retain the value c. The changes in question will follow the laws which apply to a system in which only one variable is affected by hysteresis. This system will allow of a well-defined network of ascending and descending isotherms; but *the disposition of this network will depend essentially upon the value* c *of the constant* C. To this fixed value of c there belongs a fixed position O of the point (Π, h) where the 'turning' appears for the first time; also a form and a position of the descending curve A_a which passes through this point; a form and a position for the closed cycle γ described between two given values of Π,—for example, $\Pi = 0$ and $\Pi = \pi = 12.7$ mm, etc.

Let us suppose now that the second jelly is left for a long time, say several months, under a pressure of aqueous vapor which oscillates between narrow limits about the mean value Π_0, and at a temperature similarly oscillating about a mean value T_0. The state of this jelly will gradually change; its representative point will be displaced along a line parallel to Oh in such a way that h will diminish. During such a change, the sum

$$\sum g_h(h, x, \Pi_0, T_0)|dh|$$

will have a finite value; $\Sigma|dh|$ will always have a large value, of the order of $\frac{1}{g_h(h, x, \Pi, T)}$; and furthermore $g_h(h, x, \Pi_0, T_0)$ is positive under the conditions given, so that

$$\sum g_h(h, x, \Pi_0, T_0)|dh|$$

is also positive. According to equations (41) and (42), we see that the quantity $C = F(h, x, \Pi, T)$, whose value was c before this change, has a different value c' after the change, and we have

$$c' - c + \sum g_h(h, x, \Pi_0, T_0)|dh| = 0, \qquad (50)$$

so that c' is less than c.

After this change in the second jelly, let us submit it to various transformations such that they do not together cause $\Sigma|dh|$ to assume a very large value. These transformations will follow the laws which apply to a system where only one variable is subject to hysteresis: this system will admit of a well-defined network of ascending and descending isotherms. *But this network, whose disposition depends on the value c′ given to the constant* C, *is by no means identical with the network which refers to the first jelly.* The position of the point $O'(\Pi', h')$ where the 'turning' first appears, the form and position of the descending line A'_a which passes through the point O′, the form and position of the cycle γ' described between two given values of Π as above,—all of these properties of the second jelly will differ from the corresponding properties for the first.

Experiment alone can show how these properties change when the value of the constant C is altered; and numerous observations of van Bemmelen[1] bear upon this point. They show that two cycles γ, γ', described between the same limits of pressure $\Pi = 0$ and $\Pi = \pi = 12.7$ mm, but of which the first corresponds to the value c, and the second to the value c', less than c, of the constant C, are disposed, with respect to one another, as shown in Fig. 8. The upper limit S of the cycle γ is far above the limit S′ of the cycle γ'.

Other things being equal, the difference $(c - c')$ will be larger, and consequently the cycle γ' will vary the more from the cycle γ, according as the second jelly has been kept a longer time at a pressure and temperature near to Π_o, T_o. More generally, let us suppose that any jellies originally identical have undergone any changes whatever, and different one from another. In the course of these changes, $\Sigma|dh|$ may have assumed very large values, or $g_h(h, x, \Pi, T)$ may have ceased to be very small. Then let us bring all these jellies into the field to which the foregoing considerations apply. In order to study them, we must give different values to the quantity C — and each one of the jellies may be characterized by the value of C belonging to it. Now,

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[1] Zeit. anorg. Chem. 13, 280; Fig. 9, p. 344; Figs. 12, 13, 14, pp. 347 to 349 (1896).

the observations just cited have shown in what direction we displace the cycle described between the values for pressure $\Pi = 0$ and $\Pi = 12.7$ mm, by giving smaller and smaller values to C. Inversely, by comparing the positions of this cycle for two different jellies, it is possible to deduce the order in which the values of C, belonging to these two jellies, are ranged. The higher the upper limit of the cycle S, the larger the corresponding value of C.

Let us take, for instance, two identical jellies. The first, studied immediately, gives us the cycle γ (Fig. 9); the second is dried, heated for a few moments to redness, then hydrated again and studied. It furnishes the cycle γ'. According to numerous concordant observations of van Bemmelen,[1] the sum-

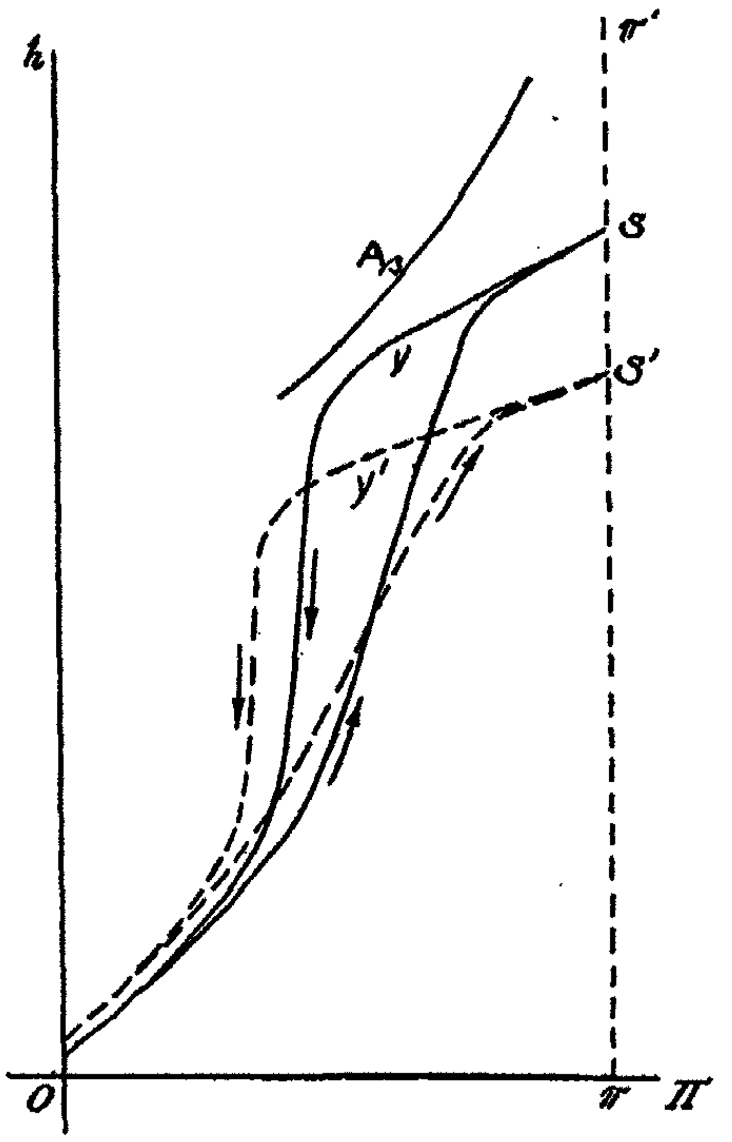

Fig. 8

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[1] loc. cit. p. 289; Fig. 14, p. 349; Figs. 15*a*, 15*b*, 15*c*, 15*d*, 15*e*, pp. 350 to 353.

mit S′ of the cycle γ′ will be far below the summit S of the cycle γ; hence by drying out a jelly and heating to redness we diminish very considerably the value of C which characterizes it. If we dry out a second time and heat again for a few moments to redness, we find, on studying the subsequent hydration, that this second treatment corresponds to a new diminution of the value of C, though the diminution in the second case is not so considerable as in the first.

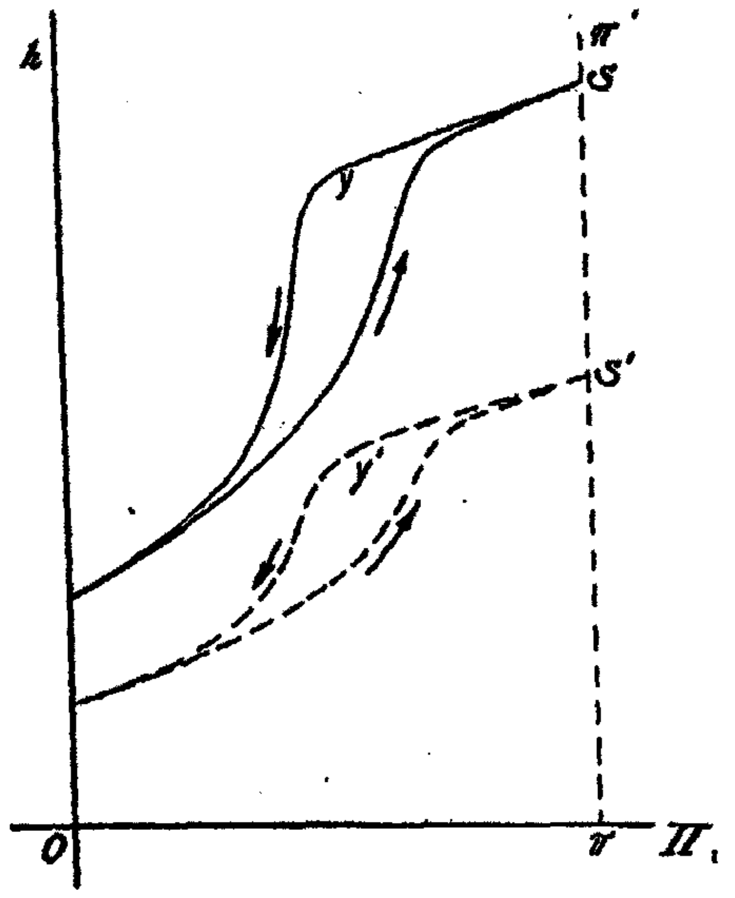

Fig. 9

Furthermore, the first operation would have produced a greater diminution of the value of C, and a greater lowering of the summit of the cycle, had the jelly been exposed to a red heat for a longer period of time, say ten minutes, instead of an instant. Hence, heating to redness has the same effect upon the jelly as exposing it for a long time to a low pressure of aqueous vapor; only the first affects it more rapidly and more intensely. Van Bemmelen[1] has clearly indicated the character of the effect

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[1] loc. cit. p. 292.

upon the jelly of heating to redness: "This action which goes on during a time counted by minutes, or even by seconds, is analogous to that which is produced at 15° with extreme slowness (requiring months or years), and with increasing slowness, by keeping a jelly which has not yet 'turned' under a low pressure. After the turning, the action is even much slower."

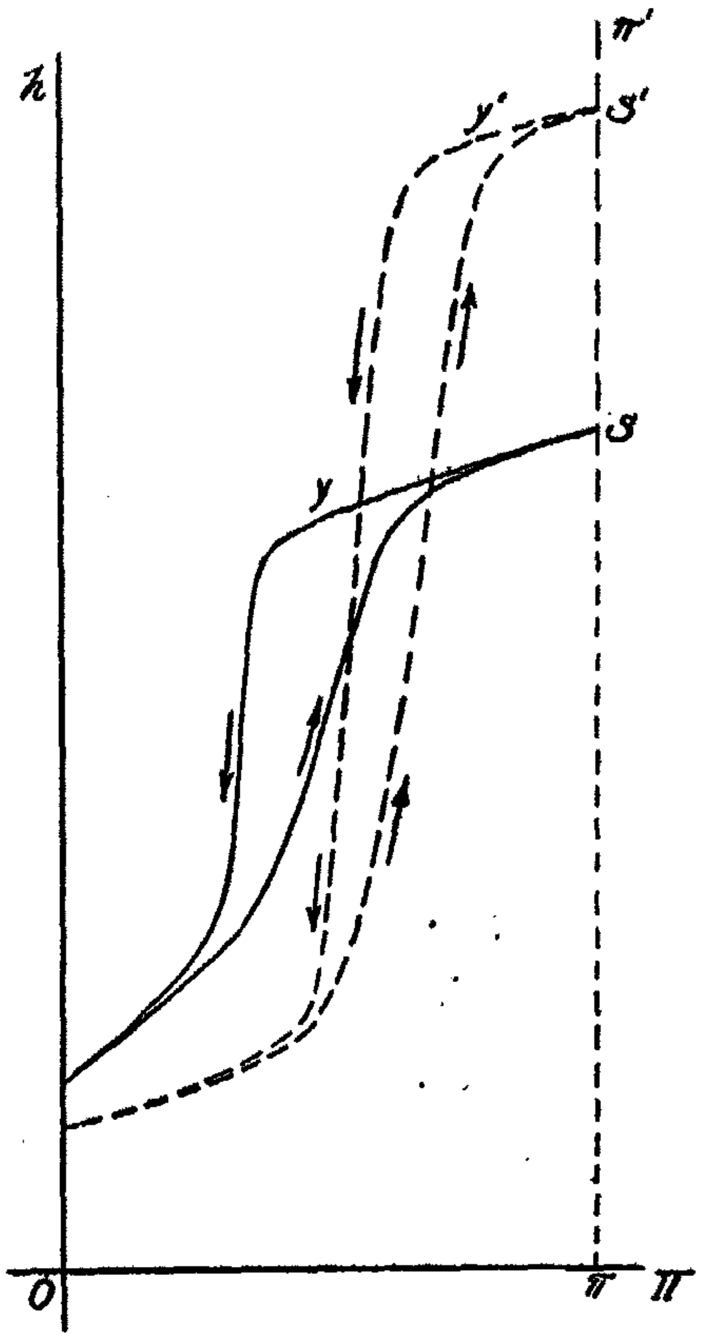

Fig. 10

Let us take two identical jellies,[1] freshly prepared. The first, immediately studied, gives the cycle γ (Fig. 10). Let us

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[1] Van Bemmelen, loc. cit. pp. 275, 283, 286; Fig. 2, p. 837; and Fig. 10, p. 345.

leave the second during several months or years in presence of saturated water vapor, or in contact with liquid water, and then let us study it in the same manner as the first jelly was studied. It yields the cycle γ'; the summit S′ of this cycle lies above the summit S of the cycle γ: the value c' of the quantity C in the case of the second jelly, is larger than the c of the first.

4. Return to the phenomena studied in Chapter I.

For the purpose of studying the phenomena of incipient dehydration, we have supposed that the state of the system depended upon only one variable affected by hysteresis, the variable h. On the other hand, in classifying the phenomena presented by a jelly in which dehydration has advanced to a certain stage, we have found it necessary to introduce a new variable affected by hysteresis, namely the variable x, and even to give it a preponderant role.

Will not this variable play a part also, though a less important one, in highly hydrated jellies? It is all the more reasonable to suppose so, because the theory developed on the basis of one variable, h, affected by hysteresis, does not represent all the facts observed by van Bemmelen in studying jellies where dehydration had been carried only a little way.

If for a given value of C we draw, as we have done above, the ascending and descending lines, we find, in the case of jellies whose hydration is greater than that which corresponds to the 'turning,' that the ascending and descending lines meet in a point, where they make an imperceptible angle with each other. Van Bemmelen represents these two lines as identical. We must conclude from this, that, at the specified degree of hydration, the function $\gamma_x(x, \mathrm{T}, \Pi, \mathrm{C})$ assumes a very small absolute value; and since, according to the second equation (44), this function is numerically equal to $g_x(h, x, \mathrm{T}, \Pi)$, we are led to the following proposition:

The phenomena studied in Chapter I. appear in systems which depend on two variables subject to hysteresis, h *and* x;

but they are produced under conditions under which the function $g_x(h, x, T, \Pi)$ ***has constantly a very small absolute value.***

The study of such systems evidently includes two distinct cases, according as the absolute value of $g_h(h, x, T, \Pi)$ is finite, or very small. Let us examine, successively, these two cases.

FIRST CASE. THE ABSOLUTE VALUE OF $g_x(h, x, T, \Pi)$ IS NEGLIGIBLE IN COMPARISON WITH THE ABSOLUTE VALUE OF $g_h(h, x, T, \Pi)$. — The case is to be treated in exactly the same way that we followed, in the present chapter, for the case where the function g_h had an absolute value which was negligible in comparison with the absolute value of the function g_x.

Equation (40) may be written

$$d\frac{\partial\phi(h, x, T, \Pi)}{\partial x} + g_x(h, x, T, \Pi)\,|dx| = 0. \tag{51}$$

Let us consider a series of changes which are not sufficiently extended to give to $\Sigma\,|dx|$ a large value, of the order of $\frac{1}{g_x(h, x, T, \Pi)}$. We can, in the course of these changes, regard the quantity K which figures in the equation

$$\frac{\partial\phi(h, x, T, \Pi)}{\partial x} = K \tag{52}$$

invariable. Solving this equation for x, we have

$$x = \xi(h, T, \Pi, K)\,; \tag{53}$$

and we put

$$\frac{\partial}{\partial h}\Big[\,(1 + h)\phi(h, x, T, \Pi) - h\Phi(T, \Pi)\,\Big] = F(h, x, T, \Pi), \tag{54}$$

$$\left.\begin{aligned} F[h, \xi(h, T, \Pi, K), T, \Pi] &= \Psi(h, T, \Pi, K), \\ g_h[h, \xi(h, T, \Pi, K), T, \Pi] &= \gamma_h(h, T, \Pi, K). \end{aligned}\right\} \tag{55}$$

Equation (39) then becomes

$$\frac{\partial\Psi(h, T, \Pi, K)}{\partial h}\,dh + \frac{\partial\Psi(h, T, \Pi, K)}{\partial\Pi}\,d\Pi$$
$$+ \frac{\partial\Psi(h, T, \Pi, K)}{\partial T}\,dT + \gamma_h(h, T, \Pi, K)\,|dh| = 0. \tag{56}$$

If K may be considered constant, this equation (56) may be treated like equation (9).

Let us treat, in particular, the following problem: At strictly constant temperature, the pressure of aqueous vapor varies, passing from Π_0 to Π_1 during the small time interval $t_1 - t_0$; but this variation is irregular, so that

$$\sum |d\Pi| = |\Pi_1 - \Pi_0| + 2\lambda. \tag{57}$$

Putting

$$V = \frac{\Pi_1 - \Pi_0}{t_1 - t_0}, \qquad D = \frac{2\lambda}{t_1 - t_0}, \tag{57 bis}$$

the velocity of hydration v_h will be given by the following formula, analogous to formula (21),

$$v_h = -\frac{\dfrac{\partial\Psi(h, \Pi, K)}{\partial\Pi}\,\dfrac{\partial\Psi(h, \Pi, K)}{\partial h}}{\left[\dfrac{\partial\Psi(h, \Pi, K)}{\partial h}\right]^2 - \left[\gamma_h(h, \Pi, K)\right]^2}\,V$$

$$+ \frac{\dfrac{\partial\Psi(h, \Pi, K)}{\partial\Pi}\,\gamma_h(h, \Pi, K)}{\left[\dfrac{\partial\Psi(h, \Pi, K)}{\partial h}\right]^2 - \left[\gamma_h(h, \Pi, K)\right]^2}\,(|V| + D). \tag{58}$$

This equation permits us to transfer to the case where the function g_x is negligible in comparison with g_h, everything that was deduced in Chapter I., from equation (21), concerning a system dependent on the single variable h.

SECOND CASE. THE TWO FUNCTIONS $g_h(h, x, T, \Pi)$ AND $g_x(h, x, T, \Pi)$ HAVE VERY SMALL ABSOLUTE VALUES. — The function $\gamma_h(h, T, \Pi, K)$ being, according to the second equation (55), numerically equal to the function $g_h(h, x, T, \Pi)$, it will have a very small absolute value. Hence we can deduce from equation (58) the conclusion:

If the function g_h *have a very small absolute value, and if* *the function* g_x *be negligible with respect to* g_h, *then the velocity of hydration will be given by the formula*

$$v_h = \omega + \epsilon_h, \tag{59}$$

where

$$\omega = -\frac{\dfrac{\partial\Psi(h, \Pi, K)}{\partial\Pi}}{\dfrac{\partial\Psi(h, \Pi, K)}{\partial h}} V, \tag{60}$$

$$\epsilon_h = \frac{\dfrac{\partial\Psi(h, \Pi, K)}{\partial\Pi}}{\left[\dfrac{\partial\Psi(h, \Pi, K)}{\partial h}\right]^2} \gamma_h(h, \Pi, K)(|V| + D). \tag{61}$$

Let us undertake now to treat the inverse problem: *Suppose the absolute value of* g_x *to be very small, and* g_h *to be negligible in comparison with* g_x.

The perceptible variations of x will follow one another with a velocity

$$u = -\frac{\dfrac{\partial^2\Psi(x, \Pi, C)}{\partial x\partial\Pi}}{\dfrac{\partial^2\Psi(x, \Pi, C)}{\partial x^2}} V$$

$$+ \frac{\dfrac{\partial^2\Psi(x, \Pi, C)}{\partial x\partial\Pi} \gamma_x(x, \Pi, C)}{\left[\dfrac{\partial^2\Psi(x, \Pi, C)}{\partial x^2}\right]^2} (|V| + D). \tag{62}$$

But we have

$$h = \mathfrak{h}(x, \Pi, C). \tag{43}$$

Hence the velocity of hydration becomes

$$v_h = \frac{\partial}{\partial x} \mathfrak{h}(x, \Pi, C)u + \frac{\partial}{\partial\Pi} \mathfrak{h}(x, \Pi, C)V\ ;$$

or, because of equation (62),

$$v_x = \omega' + \epsilon_x, \tag{63}$$

where

$$\omega' = -\left(\frac{\dfrac{\partial^2\Psi(x, \Pi, C)}{\partial x \partial \Pi}}{\dfrac{\partial^2\Psi(x, \Pi, C)}{\partial x^2}} \frac{\partial \mathfrak{h}(x, \Pi, C)}{\partial x} - \frac{\partial \mathfrak{h}(x, \Pi, C)}{\partial \Pi} \right) V, \quad (64)$$

$$\epsilon_x = \frac{\dfrac{\partial^2\Psi(x, \Pi, C)}{\partial x \partial \Pi} \gamma_x(x, \Pi, C) \dfrac{\partial \mathfrak{h}(x, \Pi, C)}{\partial x}}{\left[\dfrac{\partial^2\Psi(x, \Pi, C)}{\partial x^2}\right]^2} (|V| + D). \quad (65)$$

Let us compare the value (60) of ω and the value (64) of ω'. Because of the first equation (55),

$$\frac{\partial \Psi}{\partial h} = \frac{\partial F}{\partial h} + \frac{\partial F}{\partial x} \frac{\partial \xi}{\partial h},$$

$$\frac{\partial \Psi}{\partial \Pi} = \frac{\partial F}{\partial \Pi} + \frac{\partial F}{\partial x} \frac{\partial \xi}{\partial \Pi}.$$

Furthermore, equation (52) which, when solved, takes the form (53), gives

$$\frac{\partial^2 \phi}{\partial x^2} \frac{\partial \xi}{\partial h} + \frac{\partial^2 \phi}{\partial x \partial h} = 0,$$

$$\frac{\partial^2 \phi}{\partial x^2} \frac{\partial \xi}{\partial \Pi} + \frac{\partial^2 \phi}{\partial x \partial \Pi} = 0.$$

We have then

$$\omega = -\left(\frac{\dfrac{\partial F}{\partial \Pi} \dfrac{\partial^2 \phi}{\partial x^2} - \dfrac{\partial F}{\partial x} \dfrac{\partial^2 \phi}{\partial x \partial \Pi}}{\dfrac{\partial F}{\partial h} \dfrac{\partial^2 \phi}{\partial x^2} - \dfrac{\partial F}{\partial x} \dfrac{\partial^2 \phi}{\partial x \partial h}} \right) V. \quad (66)$$

But the first equation (44) gives

$$\frac{\partial^2 \Psi}{\partial x^2} = \frac{\partial^2 \phi}{\partial x^2} + \frac{\partial^2 \phi}{\partial x \partial h} \frac{\partial \mathfrak{h}}{\partial x},$$

$$\frac{\partial^2 \Psi}{\partial x \partial \Pi} = \frac{\partial^2 \phi}{\partial x \partial \Pi} + \frac{\partial^2 \phi}{\partial x \partial h} \frac{\partial \mathfrak{h}}{\partial \Pi},$$

while equations (42) and (43) give

$$\frac{\partial F}{\partial h}\frac{\partial \mathfrak{h}}{\partial x}+\frac{\partial F}{\partial x}=0,$$

$$\frac{\partial F}{\partial h}\frac{\partial \mathfrak{h}}{\partial \Pi}+\frac{\partial F}{\partial \Pi}=0.$$

Hence we have

$$\omega'=\left(\frac{\frac{\partial^2\phi}{\partial x\partial h}\frac{\partial F}{\partial \Pi}-\frac{\partial^2\phi}{\partial x\partial \Pi}\frac{\partial F}{\partial h}}{\frac{\partial^2\phi}{\partial x\partial h}\frac{\partial F}{\partial x}-\frac{\partial^2\phi}{\partial x^2}\frac{\partial F}{\partial h}}\frac{\frac{\partial F}{\partial x}}{\frac{\partial F}{\partial h}}-\frac{\frac{\partial F}{\partial \Pi}}{\frac{\partial F}{\partial h}}\right)V. \quad (67)$$

Making all reductions, equation (67), compared with (66), shows that for any same initial state of the system we have

$$\omega'=\omega. \quad (68)$$

Equation (43) may be solved for x, giving

$$x=\mathfrak{r}(h, \Pi, C), \quad (69)$$

an equation which may still be regarded as equation (42) solved for x. Hence we have, identically,

$$h=\mathfrak{h}[\mathfrak{r}(h, \Pi, C), \Pi, C], \quad (70)$$

which gives, by differentiation,

$$\frac{\partial \mathfrak{h}}{\partial x}\frac{\partial \mathfrak{r}}{\partial h}=1. \quad (71)$$

Let us put

$$\gamma_x[\mathfrak{r}(h, \Pi, C), \Pi, C]=\Gamma_x(h, \Pi, C), \quad (72)$$

$$\Psi[\mathfrak{r}(h, \Pi, C), \Pi, C]=\chi(h, \Pi, C). \quad (73)$$

This equation (73) gives us first

$$\frac{\partial \Psi}{\partial x}\frac{\partial \mathfrak{r}}{\partial h}=\frac{\partial \chi}{\partial h}, \quad (74)$$

then

$$\frac{\partial^2\Psi}{\partial x^2}\left(\frac{\partial \mathfrak{r}}{\partial h}\right)^2+\frac{\partial \Psi}{\partial x}\frac{\partial^2 \mathfrak{r}}{\partial h^2}=\frac{\partial^2\chi}{\partial h^2},$$

$$\frac{\partial^2\Psi}{\partial x\partial \Pi}\frac{\partial \mathfrak{r}}{\partial h}+\frac{\partial^2\Psi}{\partial x^2}\frac{\partial \mathfrak{r}}{\partial h}\frac{\partial \mathfrak{r}}{\partial \Pi}+\frac{\partial \Psi}{\partial x}\frac{\partial \mathfrak{r}^2}{\partial h\partial \Pi}=\frac{\partial^2\chi}{\partial h\partial \Pi}.$$

Because of equation (74), these last equations become

$$\left.\begin{aligned}
&\frac{\partial^2\Psi}{\partial x^2}=\frac{\dfrac{\partial^2\chi}{\partial h^2}\dfrac{\partial\mathfrak{r}}{\partial h}-\dfrac{\partial\chi}{\partial h}\dfrac{\partial^2\mathfrak{r}}{\partial h^2}}{\left(\dfrac{\partial\mathfrak{r}}{\partial h}\right)^3},\\
&\frac{\partial^2\Psi}{\partial x\partial\Pi}=\\
&\qquad\frac{\dfrac{\partial^2\chi}{\partial h\partial\Pi}\left(\dfrac{\partial\mathfrak{r}}{\partial h}\right)^2-\left(\dfrac{\partial^2\chi}{\partial h^2}\dfrac{\partial\mathfrak{r}}{\partial\Pi}-\dfrac{\partial\chi}{\partial h}\dfrac{d^2\mathfrak{r}}{\partial h\partial\Pi}\right)\dfrac{\partial\mathfrak{r}}{\partial h}+\dfrac{\partial\chi}{\partial h}\dfrac{\partial\mathfrak{r}}{\partial\Pi}\dfrac{\partial^2\mathfrak{r}}{\partial h^2}.}{\left(\dfrac{\partial\mathfrak{r}}{\partial h}\right)^3}
\end{aligned}\right\}\quad(75)$$

If we set

$$\frac{\dfrac{\partial^2\chi}{\partial h\partial\Pi}\left(\dfrac{\partial\mathfrak{r}}{\partial h}\right)^2-\left(\dfrac{\partial^2\chi}{\partial h^2}\dfrac{\partial\mathfrak{r}}{\partial\Pi}-\dfrac{\partial\chi}{\partial h}\dfrac{\partial^2\mathfrak{r}}{\partial h\partial\Pi}\right)\dfrac{\partial\mathfrak{r}}{\partial h}+\dfrac{\partial\chi}{\partial h}\dfrac{\partial\mathfrak{r}}{\partial\Pi}\dfrac{\partial^2\mathfrak{r}}{\partial h^2}}{\left(\dfrac{\partial^2\chi}{\partial h^2}\dfrac{\partial\mathfrak{r}}{\partial h}-\dfrac{\partial\chi}{\partial h}\dfrac{\partial^2\mathfrak{r}}{\partial h^2}\right)\dfrac{\partial\mathfrak{r}}{\partial h}}$$

$$=\mathrm{E}(h,\Pi,\mathrm{C}),\qquad(76)$$

and make use of equations (65), (71), (72), (75), and (76), we get

$$\epsilon_x=\mathrm{E}(h,\Pi,\mathrm{C})\Gamma_x(h,\Pi,\mathrm{C})(|\mathrm{V}|+\mathrm{D}).\qquad(77)$$

After these preliminary operations, we can attack the problem itself.

If we neglected the two factors of hysteresis g_h, g_x, or the two functions γ_h, Γ_x which are numerically equal to them, the velocity of hydration would be

$$v=\omega.$$

If we neglected the function g_x, and neglected also the square of g_h, but not that function itself, we should have, for the velocity of hydration,

$$v_h=\omega+\epsilon_h.$$

If we neglected the function g_h, and the square only of g_x, the value for the velocity would be

$$v_x=\omega+\epsilon_x.$$

Finally, a theorem which has been stated[1] and demonstrated[2] elsewhere furnishes us the following proposition:

If, without being themselves negligible, the functions g_x, g_h, *or the numerically equal functions* Γ_x, γ_h, *are so small that their squares or their product may be neglected, the velocity of hydration will have the value*

$$v = \omega + \epsilon_h + \epsilon_x,$$

or, because of equations (60), (61), *and* (77),

$$v = -\frac{\dfrac{\partial\Psi(h, \Pi, K)}{\partial\Pi}}{\dfrac{\partial\Psi(h, \Pi, K)}{\partial h}} V$$

$$+ \left\{ \frac{\dfrac{\partial\Psi(h, \Pi, K)}{\partial\Pi}}{\left[\dfrac{\partial\Psi(h, \Pi, K)}{\partial h}\right]^2} \gamma_h(h, \Pi, K) + E(h, \Pi, C)\,\Gamma_x(h, \Pi, C) \right\}$$

$$\times (|V| + D). \qquad (78)$$

In this formula, K *and* C *may be regarded as invariable during a series of changes, provided these changes are not sufficient to give to the quantities* $\Sigma|dh|$ *and* $\Sigma|dx|$ *very large values, of the order of* $\frac{1}{g_h}$ *and* $\frac{1}{g_x}$.

Now let us combine the results obtained in the two cases just considered. Formula (58) gives the value of v when Γ_x is negligible; formula (78) neglects the square of γ_h. Hence we see that: *When the function* g_x *is very small, we may, whatever the value of* γ_h, *represent the velocity of hydration by the following formula*

$$v = -\frac{\dfrac{\partial\Psi(h, \Pi, K)}{\partial\Pi}\,\dfrac{\partial\Psi(h, \Pi, K)}{\partial h}}{\left[\dfrac{\partial\Psi(h, \Pi, K)}{\partial h}\right]^2 - \left[\gamma_h(h, \Pi, K)\right]^2} V$$

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[1] Proc. Verb. Soc. Sci. phys. nat. Bordeaux. Séance 16 Mars, 1899.

[2] To appear in Zeit. phys. Chem.

$$+\left\{\frac{\frac{\partial\Psi(h,\Pi,\mathrm{K})}{\partial\Pi}\gamma_h(h,\Pi,\mathrm{K})}{\left[\frac{\partial\Psi(h,\Pi,\mathrm{K})}{\partial h}\right]^2-\left[\gamma_h(h,\Pi,\mathrm{K})\right]^2}+\mathrm{E}(h,\Pi,\mathrm{C})\Gamma_x(h,\Pi,\mathrm{C})\right\}$$

$$\times(|\mathrm{V}|+\mathrm{D}). \qquad (79)$$

Under all circumstances this formula furnishes the principal term of the part proportional to V, *and of the part proportional to* (|V| + D). *The quantities* C *and* K *can be treated as constants only when the change in question does not cause* Σ|dh| *and* Σ|dx| *to assume very large values.*

Taking a determinate set of values for C and for K, this formula will be amenable to a discussion similar in all respects to the one given in Chapter I., § 3, regarding formula (21 bis). If the two quantities D and |V| are given, there will be, for every value of Π, corresponding values of h for which the sign of v will be independent of the sign of V, and also values of h for which the sign of v will change with that of V; these two groups of values will be separated by a certain value of h; and this value of h, together with the pressure Π, will furnish the coordinates of a point on the A_8 curve of van Bemmelen, i. e., the *line of apparent equilibrium.* But, according to what has just been said, *there will be a different line* A_8 *corresponding to each set of values of* K and C.

Let us consider two jellies, initially identical; and let us bring them both under the same pressure of aqueous vapor, one immediately, the other after an extended series of changes. C and K will have different values for the two jellies; hence, at the moment when apparent equilibrium becomes established, the value of h will not be the same for both. Van Bemmelen has shown[1] that if the second jelly has been kept for a long time under a pressure of aqueous vapor greater than Π, the apparent equilibrium will correspond to a value of h, which is higher than that for the first jelly; and that this value will be the greater the longer the second jelly has been kept under the higher pressure of water vapor.

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[1] Zeit. anorg. Chem. 13, 277; Fig. 7, 342; and Fig. 8, 343 (1896).

According to the above, the phenomenon of 'turning' is produced in a jelly under dehydration, at the moment when the function $\Gamma_x(h, \Pi, C)$ ceases to be very small. So the point $O(\Pi, h)$, corresponding to this phenomenon, will change with the value of C, and thus with the alterations to which the jelly has previously been subjected — if these changes have been prolonged. This also has been observed by van Bemmelen.[1]

CONCLUSION

It will be seen that all the phenomena, in some respects so complicated, which have been observed by van Bemmelen in studying the hydration of colloidal substances, are readily interpreted and classified by means of the principles here developed regarding systems subject to hysteresis. I take occasion to remark also that all the principles in question were announced and developed by me, either before the work of van Bemmelen appeared, or very soon after; and in any case were reached quite independently of his researches. Thus the formulæ employed in Chapter I., after having served for the study of the phenomena of rupture and recalescence, furnished also the interpretation of the properties of irreversible nickel steels, discovered by Guillaume, and of the observations of Max Wien on magnetic viscosity. As to the analysis developed in Chapter II., it is simply an application of the methods which I originated for the discussion of changes in systems dependent upon two variables affected by hysteresis. It is well known what use was made of them by Marchis in clearing up the complex facts regarding *the displacement of the zero of mercury thermometers.*

The preceding researches seem to me to confirm indirectly the conclusions reached by Marchis. They contain the direct proof of certain laws of which Marchis, from the nature of the method employed, could only verify certain consequences. To mention only one of these laws: If a system depends on two variables subject to hysteresis, h and x, and if the coefficient of

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[1] loc. cit.

hysteresis of h is very small with respect to the coefficient of hysteresis of x, then the system, when submitted to cyclical actions from without, tends to describe a *pseudo-limiting cycle*; but, *instead of remaining rigorously fixed, this cycle is displaced and deformed if perturbations of sufficient extent be brought to bear upon the system.*

Cabrespine. Sept. 15, 1899.

THE MELTING-POINT OF FORMYL PHENYL ACETIC ESTER

BY C. G. L. WOLF

As Wislicenus has shown,[1] formyl phenyl acetic ester exists in two modifications, one of which, the true formyl compound, is solid at ordinary temperatures and partly changes on heating above its melting-point into the second modification, which so far has not been obtained in the solid condition. The melt resolidifies on standing after different lengths of time, depending on the amount of tautomeric change which has taken place. As the change from the liquid to the solid modification takes place at room temperature, the stable triple point, where the solid is in stable equilibrium with solution and vapor, must be between room temperature and the melting-point.

Formyl phenyl acetic ester can be made to melt at temperatures varying from 60° to 70° if the operation be carried out in melting-point tubes in the ordinary way. If the heating be rapid, the thermometer will indicate 80° before the substance is completely melted, and Brühl has even given the melting-point as 90° without giving any explanation. The point at which no change takes place is a definite one. If sealed capillary tubes containing the substance be heated in a bath regulated with a thermoregulator and well stirred, fusion occurs at any point above 50° providing the heating be sufficiently prolonged. Below this temperature, the solid modification persists and this is therefore the stable triple point.

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[1] Ber. chem. Ges. Berlin, **20**, 2933 (1887); **28**, 767 (1895); Liebig's Ann. **291**, 147 (1896).

The pure formyl phenyl acetic acid was heated to 100° for some hours in order to obtain a concentration equilibrium at this temperature and cooled rapidly in a slush of solid carbon dioxid and ether. The temperature of the freezing mixture was – 80° on the toluene thermometer. The substance set to a glass which did not crystallize on continued rubbing. On removing the tube from the freezing mixture, the liquid melted and was apparently unchanged. At the end of twenty-four hours crystals appeared which were tested in order to ascertain whether the substance was the solid formyl compound or was the enol modification. After washing carefully with benzol and drying on a porous plate, the substance gave no color with ferric chloride and was therefore the formyl compound.

The cooling of the ester to a low temperature had thus a marked effect in hastening the crystallization of the solid modification. Under ordinary circumstances, the formyl phenyl acetic ester heated to 100° for some time, requires weeks for crystallization to take place, although Wislicenus points out that the ester contained in a flask which is opened at various times may deposit crystals in the course of a few hours;[1] but this is certainly an exception to the general rule. According to Brühl (note, ibid) the solubility of the formyl compound in the liquid is small, so that the amount of change which takes place must be great at 70°, for, when the solid is melted at that temperature, and inoculated with a crystal of the formyl compound, but little of the latter separates out and the complete solidification of the liquid takes weeks owing to the slow velocity of the reverse change.

In order to understand the change which takes place in the melt it will be necessary to refer to a diagram. Let A represent the melting-point of the solid formyl phenyl acetic ester which lies above 80°, B the unknown melting-point of the enol modification, C the eutectic point of the two isomers, and X[2] the

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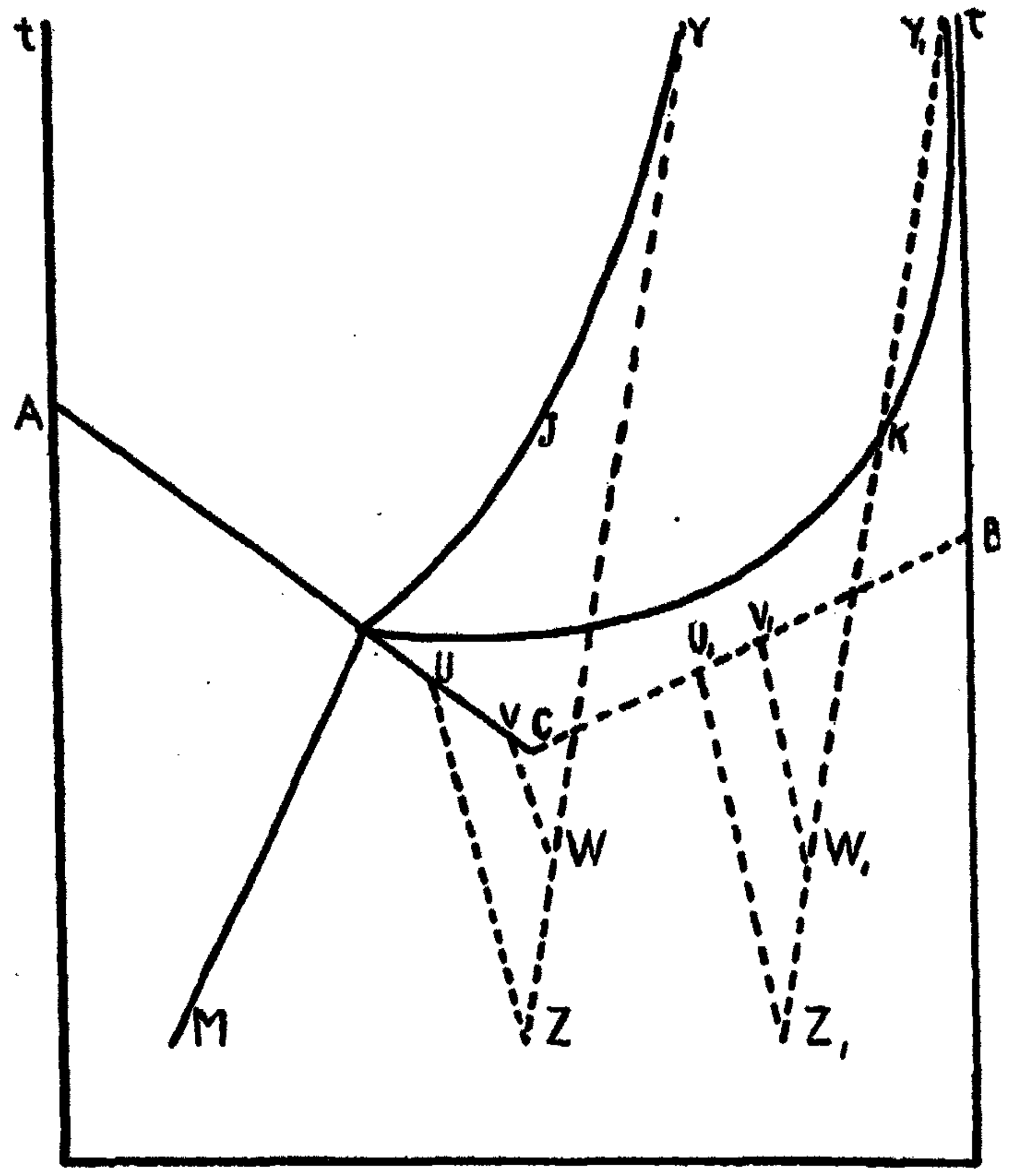
[1] Liebig's Ann. 291, 166 (1896).

[2] In the diagram the letter X should come at the intersection of MY and AC.



stable triple point for A. Y is the point above the melting-point of A which in the case cited was 100°. M represents the equilibrium concentration at — 80°. On heating A to the temperature Y, one would obtain a corresponding equilibrium. On allowing the temperature of the mixture to fall one obtains an instable point on the eutectic side of X because, when the mixture is sown with the crystals, the mass does not solidify. The equilibrium is not reached at a low temperature for the same reason, and, further, the velocity of reverse change must be slow. Hence the composition of the supercooled melt cannot be that of the equilibrium point but must be at some instable point such as Z. If then the temperature be lowered to Z, the equilibrium must be displaced towards A, or in the case of oxymethylene phenyl acetic ester the melt, although not saturated with respect to A, is considerably more, than when simply allowed to fall to room temperature, as the rate of crystallization shows. On allowing the melt to rise to room temperature, one also gets a displacement of the concentration towards A, and hence at this point the relative amounts of the two isomers will be represented by U. Similarly if the temperature fell to W and were allowed to rise again one would obtain a corresponding amount of change represented by the concentration at V.

In other words, from the experimental data which formyl phenyl acetic ester has given one has obtained the saturation of the melt with respect to the formyl phenyl acetic ester more rapidly by cooling to a low temperature and allowing the temperature to rise slowly than if the melt were simply allowed to fall to the temperature of the room and to stay there. Since the velocity of reaction usually decreases with falling temperature, other things being equal, equilibrium should be reached more slowly by lowering and raising the temperature than by keeping it constant at the higher level.

In the case of tautomeric substances, however, another factor may enter into the reaction. The tendency to change in the melt from one substance to the other is more rapid the greater the difference between the actual point of instable equilibrium and the true equilibrium. Hence, other conditions being the same, the change would take place with greater speed at the temperature Z than at the higher point W. Against this one has to set the velocity of reaction which is ordinarily slowed by a lower temperature.

If on the other hand the potential difference were sufficient to overcome the slowing due to the temperature alone, then by alternately lowering the temperature and allowing it to rise, one would be able to hasten the saturation of the melt with the solid form to a greater or less extent depending on the amount of the change due to the action of the difference in the two factors.

The case is of interest because it shows that, in cases where tautomeric change takes place, repeated cooling may hasten the saturation point, and consequent crystallization.

That cooling to a low temperature does increase the apparent reaction velocity in some cases is shown by the results of Reicher and of Pope.

Reicher found with monoclinic sulfur that the change from this modification to the rhombic form took place with increasing velocity as the temperature fell from 95° to 35°, but below this point the rapidity of the conversion was decreased with falling temperature. So enormously did the lowering of the temperature affect the rate of change that at — 35°, transformation was only accomplished in 500 times the length required at room temperature.[1] It is possible with formyl phenyl acetic ester that these low temperatures correspond to the interval between 95° and 35° in Reicher's case.

Pope[2] also shows that the rate of change in the crystallization of chloral hydrate from the form which separates out on sudden cooling to that which results on long standing is 12 times more rapid at — 18° than at ordinary temperature.

This is not exactly analogous to the case of formyl phenyl acetic ester because in Pope's work the change is taking place in the solid state, whereas here we are dealing with the field for supercooled solution, but the analogy is sufficiently good to warrant mention.

In connection with the change which takes place above the triple point, two curves may represent the line of equilibrium. Brühl has assumed, in treating the change of formyl phenyl acetic ester into oxymethylene phenyl acetic ester, that at a comparatively low temperature the tautomeric change is great, and indeed in his later work has asserted that a complete transformation occurs.[3] That this is not true is evident from a consideration of the law of mass action, for equilibrium is always reached

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[1] Recueil Trav. Pays-Bas. 2, 251 (1883); 3, 1 (1884).

[2] Jour. Chem. Soc. 75, 455 (1899).

[3] Zeit. phys. Chem. 30, 62 (1899); Ber. chem. Ges. Berlin, 32, 2326 (1899).

with both components in the melt. Should however the greater part of the change take place at low temperatures the equilibrium curve for the two forms in the solution would follow the general line of the curve XKY_1. If the change took place more gradually with an equal increment of temperature the curve would rise more vertically from the origin, and take the form XJY. From any experiments which have been made with formyl phenyl acetic ester no conclusions can be drawn as to the form of this curve. Attempts have however been made in this direction by observations of the length of time taken to obtain a saturated solution after heating for various periods and at various temperatures above the melting-point of the substance, and Wislicenus has shown[1] that crystals heated but a short time above 70° recrystallize more rapidly than those which have been heated for an hour at 80°.

This of course points more to the change not being instantaneous than to the completeness at the two points.

It would appear from theoretical considerations that an estimate of the temperature at which the greatest amount of change takes place could be deduced from the apparent specific heat.

As the transformation of the formyl compound into the oxymethylene derivative takes place with absorption of heat, this absorption must be a measure of the amount of change taking place. Should one therefore determine the specific heat for the solution between 50° and 55° and follow calorimetrically the amount of heat necessary to raise the temperature of the melt through a definite range, one should find that if the curve had the general form XJY the heat of change would be distributed approximately equally along the length of the curve. If on the other hand the greater amount of change took place at a low temperature, and should one attempt to raise a given weight of the liquid through a definite temperature interval starting at 50°, then the amount of heat would be equal to the specific heat plus the heat of reaction. In the case of the curve

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[1] l. c. page 170.

XJY_1 the amount of heat necessary to raise the liquid through the temperature range above K would be less than below that point, provided that the specific heat did not vary with the temperature, which is, of course, strictly speaking, not the case.

Cornell University.

FREEZING-POINT CURVE FOR WATER CONTAINING HYDROCHLORIC ACID AND PHENOL

BY J. A. EMERY AND F. K. CAMERON

In the work here described, the mass of water was always relatively large as compared with the masses of hydrochloric acid and phenol. The amount of water and hydrochloric acid dissolved in the phase liquid phenol was always small, and consequently the separation of solid phenol on cooling, affected the concentration of the hydrochloric acid in the water to an entirely negligible extent.

A series of solutions was prepared from pure hydrochloric acid and distilled water, ranging in concentration from pure water to about a half normal (*n*/2) solution. The strength of this last solution was carefully determined gravimetrically, the chlorine being weighed as silver chlorid. The solution thus prepared was taken as the standard, and compared with each of the others by titration against a solution of sodium hydroxide. A series was made by each of us separately. The column marked " E " in the table was calculated from determinations made by titrating against a weak solution about (*n*/10) of alkali, with phenolphthalein as indicator. The column "C" was obtained by titrating against a relatively strong about (*n*/2) solution of alkali, using cochineal as indicator. The burettes were not calibrated, but the determinations, using widely varied amounts of solution and from different parts of the instruments, compared very well with one another.

The freezing-points were determined with the Beckmann apparatus, using differential thermometers made by Goetze.

Here again a separate series was made by each of us with different instruments. For the determinations in column E, the thermometer used was a very fine one with large bulb and capillary. It "set" very readily. In the other series C, the thermometer had a short stout bulb with very fine capillary. Both instruments were graduated to hundredths of a degree (0.01° C) and thousandths were readily estimated with a glass, using all due precautions in making the readings. The determinations compared well together, the variations being about equally distributed as to sign, so it was not deemed worth while to calibrate the instruments.

The phenol was purified by distillation, first and last portions being discarded. It was carefully kept in a flask with a closely fitting stopper carrying a calcium chlorid drying tube. When needed it was melted over a Bunsen flame, the desired amount withdrawn by a pipette and quickly transferred to the solution under examination. About 1.5 cc of liquid phenol to 20 cc of the hydrochloric acid solution was the proportion generally used.

The freezing-points were determined as follows: The solution prepared as just described was introduced into the instrument and cooled in the usual manner with occasional stirring. The mercury would fall regularly. After more or less undercooling had taken place, the separated phenol would rather suddenly solidify, which would be accompanied by rapid rising of the mercury in the thermometer. The rise would be but momentary, and the mercury would commence to fall again about as rapidly, but apparently more regularly than before the separation of the solid phenol.

The undercooling, separation of ice and rise of the mercury to the freezing-point would proceed as usual. For the first determination in each case, the amount of supercooling was generally large (2°–4°) and the reading somewhat low, but much less than previous experience with the method would have led us to expect. The tube containing the solution would be withdrawn from the freezing bath, warmed until the temperature had risen 2°–3°, being thoroughly shaken meanwhile; and again placed in the bath of freezing mixture. The subsequent readings were generally made with but little (about 0.5° on the average) previous undercooling. The readings compared very well with one another. When a sufficient number of satisfactory readings had been obtained, the apparatus was carefully cleaned, distilled water introduced, and its freezing-point determined. The difference between the freezing-points of the solution and pure water was the reading recorded. This method was followed in every case. The barometric readings were taken from time to time during the determinations. In every case recorded here, the variation in this respect was quite small and could have had no appreciable effect on the determination. Every effort was made to prevent prejudiced readings. The freezing-point determinations were all completed before the concentrations of the solutions were known, and all the experimental data were obtained before any attempt was made to tabulate or chart them. It seems proper to say that we regard the amount of hydrochloric acid given under C as the more reliable, while the freezing-points under E are to be given the preference. In Table I the first pair of columns record the grams hydrochloric acid per liter of solution. The second the number of reacting weights per liter of solution. The third the corresponding freezing-points on the centigrade scale. We have in our possession some data for more concentrated solutions than those tabulated

TABLE I

E	C	E	C	E	C
0.0000	0.0000	0.0000	0.0000	—1.179°	—1.177°
0.8832	0.8668	0.0242	0.0233	—1.267	—1.268
1.6040	1.6295	0.0440	0.0447	—1.340	—1.334
2.5437	2.5565	0.0698	0.0701	—1.436	—1.424
4.4798	4.5273	0.1229	0.1242	—1.636	—1.710[1]
8.6349	9.0436	0.2369	0.2481	—2.077	—2.077
18.2478	18.2478	0.5006	0.5006	—3.007	—3.010

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[1] Unfortunately, through the breaking of the mercury column, a *direct* comparison with the freezing-point of water was not possible in this case alone.

above. All our results when charted fall on or very close to a straight line.

But the data for these more concentrated solutions are not given here, as we regard them as very unsatisfactory. The determinations made by each of us separately vary nearly 5 percent in some cases, nor do the individual readings compare more favorably with one another. As an example, for a solution containing 26.7695 gms of hydrochloric acid per liter, one of us found the freezing-point to be – 3.788°; the other found it to be – 3.973°; the average of these would be – 3.880°, the computed value being 3.855°. While the variation in our observations is about 4.6 percent, the error in the average is less than 1 percent, corresponding to less than 0.25 gms hydrochloric acid per liter of solution.

Starting from the same initial temperature and with the same amount of undercooling, fairly concordant results would be obtained. But slight variations in either of these particulars would cause wide variations in the readings. That the instruments were not at fault was shown by the excellent results in obtaining the freezing-point of water at the same time. The work was unfortunately interrupted before this difficulty could be thoroughly investigated.

The comparison of our results with those obtained for hydrogen chlorid and water alone is interesting. In Table II the first column represents reacting weights per liter; the second the corresponding depression of the freezing-point found; the third the lowering of the freezing-point per reacting weight of hydrogen chlorid in a liter of solution. In Table III similar

TABLE II

0.0238	0.088°	3.672°
0.0447	0.161	3.601
0.0701	0.257	3.666
0.1242	0.457	3.679
0.2481	0.898	3.619
0.5006	1.828	3.651
		3.648 average

TABLE III

0.0136	00.5°	3.676°
0.0409	0.15	3.667
0.0546	0.20	3.663
0.0838	0.30	3.579
0.0982	0.35	3.564
		3.630 average

data are presented calculated from the results of Jones for hydrochloric acid and water. It will be noticed that the depression of the freezing-point for a reacting weight of hydrochloric acid per liter of solution is a constant. And in both cases the constants agree with one another well within the possible errors of experiment. It follows that the curve in each case is a straight line, and the curves are parallel. This simply means that within the temperature range involved the solubility of phenol in water is practically constant, and the consequent lowering of the freezing-point is a purely additive effect.

To sum up:

I. The freezing-point of water, saturated with respect to phenol is — 1.179° C.

II. The freezing-point curve for solutions of hydrogen chlorid in water is a straight line. The freezing-point curve for aqueous solutions of hydrogen chlorid saturated with respect to phenol is a straight line, and

III. The curves just mentioned are parallel, i. e. the depression of the freezing-point of water by hydrogen chlorid and phenol, under the conditions described, is an additive effect.

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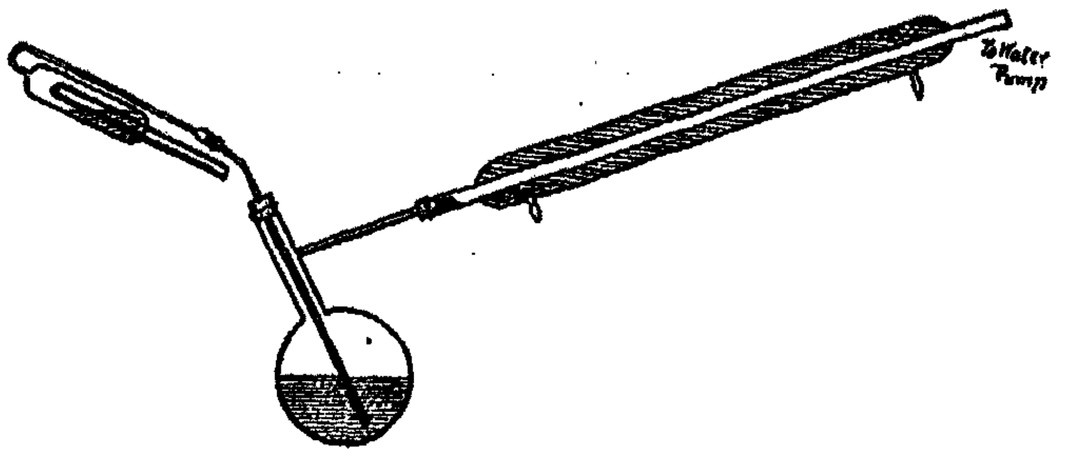
NOTE ON BUNSEN'S ICE CALORIMETER

BY J. W. MELLOR

The complete separation of dissolved air from the water used in making the "ice kernel" in Bunsen's calorimeter is necessary for accurate results, as was pointed out by Bunsen himself.[1] At any time the separation of air from water so that the latter will give the characteristic "click" is a difficult matter, while the filling of the above calorimeter with such water is a still more tedious operation.



The simplification introduced by Wadsworth[2] gives a fair approximation; while the following simple device requiring little or no attention gives a splendid result.

The end of a Liebig's condenser is fitted to the side neck of an ordinary liter distilling flask, and the other end is connected to a water air-pump.[3] The flask is about half filled with distilled water, and the outer chamber of the calorimeter is about one-

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[1] Bunsen. Pogg. Ann. 141, 1 (1870). Cf. also Schuller and Wartha. Wied. Ann. 2, 359 (1877).

[2] Wadsworth. Amer. Jour. Sci. [4] 4, 265 (1897).

[3] Cf. Ostwald. Manual of Physico-Chem. Measurements, 175 (1894).

third filled with distilled water. A tube dipping almost to the bottom is fitted into the neck of the distilling flask and also into the opening of the side tube of the calorimeter, as shown in the figure.

The pump is set in action, and the water in the calorimeter is heated by a Bunsen flame with a sheet of asbestos placed between the flame and the glass. The flask is heated over a sand-bath until its contents give the characteristic "hammering" when shaken. The lamp is then removed from under the calorimeter and the latter will very soon be filled with air-free water.[1]

The troublesome bumping of water boiling under reduced pressure is considerably mollified by the tube dipping under the water in the flask.

Owens College, Manchester

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[1] The mercury may be added as recommended by Ostwald, l. c.

NEW BOOKS

Cinématique et Mécanismes; *Potentiel et Mécanique des Fluides. Cours professé à la Sorbonne. By H. Poincaré. Rédigé par A. Guillet. 16 × 25 cm; 385 pp. Paris: Carré et Naud. 1899. Price, 15 francs.* — Someone has stated that Alexander von Humboldt was the last man possessed of a complete command of the science of his own day. Looking at the present volume, however, which is the thirteenth of a series on physics and applied mathematics, written by a man eminent in pure mathematics and astronomy, one is little induced to enter into comments of the above nature; for there is no telling where Poincaré's prolific authorship may not lead. All his textbooks are simply and fascinatingly written and have been deservedly welcomed. Many of them, like the Thermodynamique, the Électricité et Optique, etc., have already entered American universities as textbooks. The present volume is no exception in the series. The student fond of the geometry of motion, in particular the engineer (to whom the book as a whole is addressed), will find here a singularly clear and smoothly written treatise, possessing a markedly original flavor throughout. Unfortunately pure kinematics is always a little disappointing, so long as the reader is aware that dynamics, though somewhat more cumbersome, is so much more efficient from the practical point of view. This is the general impression left after a perusal of the first part of the work, relating to translation, rotation in two and three dimensions, relative and helical motion. A brief chapter on elementary machines follows.

Apart from the manner of presentation, the chapter on the Newtonian potential differs from the classic monograph of Clausius chiefly in terminology. Lines of force, flux of force, etc., are terms now as familiarly used in France as elsewhere. It is pleasant to note that Poincaré has adopted the round delta of Jacobi to designate partial differential coefficients, an innovation in French textbooks. Ample treatment is accorded to Green's Theorem, and unusually much space to the attraction of ellipsoids.

Hydrostatics includes barometry and flotation, the latter illustrated with many examples. In hydrodynamics the usual equations are derived, with brief mention of gravitational waves, and a final chapter on the chief properties of vortices.

C. Barus

Chemistry: its Evolution and Achievements. *By F. G. Wiechmann. 12 × 18 cm; pp viii + 176. New York: William R. Jenkins, 1899.* — "It seems to the writer that space might be found on the bookshelves of lovers of knowledge for some modest volumes, which, without wish or pretense to displace any learned treatises on the topics they discuss, would offer to their readers a correct and concise synopsis of the subjects they consider.

"Works of this description, — science sketches would seem an appropriate designation for them,—should prove welcome to all who take a general interest in science. ...

"Some knowledge of the various phases through which a science has passed is, moreover, of value in teaching one to place a more just — perhaps it were better to say, a more modest — estimate on the theories of the day. For, while it is indisputable that a truth once discovered is never lost, although the form in which it is embodied may be altered, yet it is also beyond question that doctrines and dicta pass away, even as the men who formulate and pronounce them."

The writer has made an interesting and readable book, the only fault with it being that it is too brief. *Wilder D. Bancroft*

L'Oeuvre de M. J. van 't Hoff. *À propos d'un livre récent. By P. Duhem. 17 × 25 cm; 27 pp. Paris: A. Hermann, 1900.* — The present pamphlet is a reprint of the last of a series of brilliant popular articles, on different branches of physical chemistry, which Duhem has contributed during recent years to a French journal of popular science, the *Revue des Questions scientifiques.* Previous brochures have treated: The Atomic Notation and Atomistic Hypotheses (1892), Reflections on Experimental Physics (1894), The Evolution of Physical Theories (1896), Thermochemistry (1897), the Phase Rule (1898), and Physical Chemistry (1899). The present article gives a popular account of the scientific work of J. H. van 't Hoff, subsuming this under the three heads: Stereochemistry, The Displacement of Chemical Equilibrium with Changing Temperature, and the Theory of Dilute Solutions. It is an enthusiastic tribute of recognition from one strong man of science to the genius of another. *J. E. Trevor*

Organic Chemistry. *By Victor von Richter. Edited by Prof. R. Anschütz. Authorized translation by E. F. Smith. 3rd American from the 8th German Edition. Vol. I. Chemistry of the Aliphatic Series. Philadelphia: P. Blakiston's Son and Co., 1899. Price, cloth, $3.00.* — The aim of the authors of this standard work is to present, in as condensed a form as possible, a complete account of the whole subject matter of organic chemistry. The continuous rapid addition to the material of this science has thus compelled a corresponding increase in the size of successive editions of the book; until at last its divisions into two volumes has been found necessary.

A comparison with the fifth edition (published in 1888) serves to remind one that it is not in the collection of facts alone that the advances made through the last decade consist. In the fifth edition, for instance, stereochemical theories are passed over with a paragraph in the introduction, even the well-known enantiomorphous tetrahedral figures not being considered worthy of reproduction; while the methods of determining molecular weights in solution are, naturally enough, omitted altogether. Few could forsee that, within the year, Prof. V. Meyer's papers on the benzil oximes would make these two matters the chief topic of discussion among organic chemists.

The present edition contains an introduction of fifty-six pages dealing with the analysis, molecular weight determination, constitution, and nomenclature of the carbon compounds; followed by twenty pages on their physical properties and behavior toward heat, light, and electricity. On p. 73, the phrase 'energy of a reaction' is, unfortunately, used as an equivalent for 'the rate at which the reaction proceeds.'

Following V. Meyer and Jacobson, the members of homologous series are, as far as may be, arranged in tables with their formulæ and physical constants; and the descriptive part is enriched by paragraphs on the technical application of the paraffins, fats, oils, etc., and by historical notes on acetoacetic acid, guanidine, the nitriles, etc. The Geneva nomenclature is applied where possible; the references to the literature are very full; and the book closes with an index of thirty-seven pages.

The appearance of the second edition of von Richter's *Chemie der Kohlenstoffverbindungen*, in 1880, was greeted by Prof. Kolbe with a scathing article entitled: "*Wie man ein chemische Lehr und Handbuch schreibt*". Paragraph after paragraph from the offending textbook was quoted, adorned with exclamation points, and followed by comments such as: "*Das ist kein Deutsch und nicht verständlich!*" "*Das schreibt ein deutscher Universitätsprofessor!*" or by caustically worded instructions in the proper use of *für* and *vor*. An attack such as this would nowadays hardly be tolerated, even were the eccentric professor still alive to make it; the labor of compiling, or even of translating, a work like this is so great that every allowance must be made for faults in literary style, consequent on extreme fatigue. Scattered throughout the book, however, sentences may be found fully equal to any quoted by Kolbe. In the hope of keeping it out of a subsequent edition, one of the worst is here printed (from p. 242): "*Acetic ether is the starting-out material for the obtainment of acetoacetic ester.*"

W. Lash Miller

Résistance électrique et Fluidité. (*Encyclopédie scientifique des Aide-mémoire.*) *By Gouré de Villemontée. 12 × 19 cm; 188 pp. Paris: Gauthier-Villars, 1899. Price, cloth 3, paper 2.50 francs.*—The other volumes of this series have all been condensed expositions of subjects which are treated at greater length in larger treatises. This volume is rather an original essay. The author tries to prove that the product of the electrical conductivity into the coefficient of viscosity is proportional to the concentration and independent of the temperature. While the book is very interesting reading, one would feel more satisfied as to the soundness of the argument if the author had not accepted Bouty's conclusion that the molecular conductivity of very dilute solutions is independent of the nature of the solute. *Wilder D. Bancroft*

Physikalische Zeitschrift. *Edited by E. Riecke and H. Th. Simon. 20 × 28 cm. Leipzig: S. Hirzel. Price, 5 marks per quarter year.*—In October of last year the first number of a weekly journal of physics was issued by its editors, Prof. E. Riecke and Dr. H. Th. Simon of the University of Göttingen. The object of the new publication is to supplement the monthly journals by the prompt publication of preliminary communications, of occasional lectures on physical topics, of reports on work in other subjects but bearing upon physics, of book reviews, of accounts of new laboratory equipments and laboratory devices, and of personal items of academic interest. The numbers that have already appeared contain much interesting matter, and it is to be foreseen that the new journal will prove a very welcome addition to the periodical literature of physics. *J. E. Trevor*

Les Sucres et leurs principaux Dérivés. *By L. Maquenne.* (*Bibliothèque technologique*), *14 × 21 cm; ii + 1032 pp. Paris: Georges Carré et C. Naud, 1900. Price, cloth, 16 francs.* — By reason of the amount and importance of the work done on the sugars and their derivatives it has become absolutely necessary that an epitome of the results should be made which would bring the literature up to a comparatively recent date. This has not been done since the appearance of the work of Tollens which came out some years ago. Maquenne has done this and has done it well. The book has a number of references that will compare favorably with any work of its kind that has been published of late years. Questions of discussion such as the birotation of the sugars, and the constitution of the saccharoses have not been dealt with as if the results were settled, but the views of those who have taken part in the discussion have been clearly and simply given and the reader is allowed to exercise his own judgment in the matter. With regard to the nomenclature, a somewhat novel idea has been introduced. The carbon atoms are numbered and those which show asymmetry are placed as are the numerals in a fraction. Thus *d*-mannite is expressed as hexanehexol $1\,\frac{4.5}{2.3}\,6$. The isomeric dulcite is hexanehexol $1\,\frac{2.5}{3.4}\,6$. This notation has the advantage of showing clearly the existence of an optical isomer. For with C_n those substances in which the sum of the numerals is a multiple of $n + 1$ or $\frac{n+1}{2}$ (where n is odd or even) will be inactive, while those which do not conform to this rule will occur in two optically active modifications. The subject index is complete, but an index of authors would have added materially to the usefulness of the book. *C. G. L. Wolf*

Les Matières odorantes artificielles. *By George F. Jaubert.* (*Encyclopédie scientifique des Aide-mémoire.*) *12 × 19 cm; 190 pp. Paris: Gauthier Villars. Price: paper $2.50, boards 3 francs.* — This is one of the series of Aide-mémoire published by Léauté and contains most of the synthetic compounds connected with perfume. Short notes of the preparation, literature, and physical and chemical properties are given. *C. G. L. Wolf*

The Urine and the Clinical Chemistry of the Gastric Contents, the Common Poisons, and Milk. *By J. W. Holland. Sixth edition, revised and enlarged. 12 × 19 cm; 124 pp. Philadelphia: P. Blakiston's Sons and Co. Price: cloth, $1.00.* — This is a small pocket book intended for clinical purposes only, and fulfils its purpose very satisfactorily. Due importance is given to methods of using the centrifuge in the various examinations which the medical student and practitioner so often make. It is curious that, amongst the number of very excellent clinical tests which the author has given, the estimation of uric acid by means of a standard piperidin solution and the detection of mercury in urine by precipitation with zinc dust should have been omitted. *C. G. L. Wolf*

REVIEWS

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

General

Revision of the atomic weight of cobalt, III. *T. W. Richards and G. P. Baxter. Proc. Am. Acad.* 35, *61; Zeit. anorg. Chem.* 22, *221* (*1899*). — Analysis of cobaltous chlorid gave 59.045, a value that is certainly a trifle high since the cobaltous chlorid contained traces of impurity, and the possible errors would all tend to raise the apparent value. All attempts to get thoroughly satisfactory results from cobaltous oxid were futile, since it proved impossible to make absolutely pure cobaltous or cobaltic oxid even though the authors took into account the dissociation pressures of both oxids. The values thus obtained varied between the extremes of 58.93 and 59.06. The value obtained from cobalt bromid, 58.995, is therefore taken as the most probable. The struggle with the oxids, though not crowned with complete success, is most instructive and has a further value in throwing much light on the sources of error in the earlier determinations. *W. D. B.*

A revision of the atomic weight of cobalt, II. *T. W. Richards and G. P. Baxter. Zeit. anorg. Chem.* 21, *250* (*1899*). — Reviewed (3, 169) from Proc. Am. Acad. 34, 351 (1899).

A revision of the atomic weight of nickel, II. *T. W. Richards and A. S. Cushman. Zeit. anorg. Chem.* 20, *352* (*1899*). — Reviewed (3, 169) from Proc. Am. Acad. 34, 327 (1899).

On a radioactive substance. *E. de Haën. Wied. Ann.* 68, *902* (*1899*). — This is a brief note stating that the author has prepared two radioactive substances from uranium which correspond to "Radium" discovered by Curie and his wife and that described by Elster and Geitel. *H. T. B.*

Reply to G. W. A. Kahlbaum. *U. Dühring. Zeit. phys. Chem.* 29, *730* (*1899*). — The author protests against a misquotation of himself by Kahlbaum (Zeit. phys. Chem. 26, 581) in which he was made to appear to depreciate the graphic method of interpolation. *A. P. S.*

Process for generating high temperatures. *H. Goldschmidt. Zeit. Elektrochemie,* 6, *53* (*1899*). — Description of the aluminum powder process and of the modifications made necessary by the different applications. *W. D. B.*

Thermometric corrections. *F. Grützmacher. Wied. Ann.* 68, *769* (*1899*). — This paper is a communication from the Reichsanstalt and is largely a recapitulation from previous papers both by the author and others. Tables for the reduction of mercury thermometers from Jena glass 16^{III} and 59^{III} to the air and hydrogen thermometers are given between 0° and 300^{c}. A table giving between 0° and 100° the difference between the correction to the hydrogen and to the air thermometer shows the maximum difference to amount to only about a hundredth of a degree. Part of the paper is devoted to enumerating the various errors in mercury thermometers and the method of comparing with the standard thermometer at the Reichsanstalt. Thermometers made from Jena glass 59^{III} show a freezing-point depression of only 0.03° for a temperature change of 100^{c}.
H. T. B.

On the air thermometer at high temperatures. *L. Holborn and A. Day. Wied. Ann.* 68, *817* ; *Am. Jour. Sci.* 8, *165* (*1899*). — The authors seem to consider that the inherent experimental difficulties attendant on high temperature measurements are not sufficient to account for the existing discrepancies, such for instance as in the melting-point of gold, and they leave an unpleasant impression as to the reliability of the work of previous observers. As far as this impression might apply to the high temperature measurements of Holborn and Wien, it is perhaps not altogether unwarranted, as has been shown by Mr. H. M. Tory in the British Association report of 1897, but to include all previous observers in this category and to throw doubt on all previoustemperature scales for the reason given is entirely misleading. Apart from this the paper is an interesting contribution to the subject and the authors seem to have taken great care in their measurements. Their study includes bulbs of Jena glass No. 59^{III} up as far as 500° with hydrogen gas, from 500^{c} to 1100° with porcelain bulbs glazed on the inside and out, and on the outside only, and the use of a platin-iridium bulb over the whole range and up as high as 1300°. Nitrogen gas was substituted for hydrogen at the higher points as the latter was found to attack the porcelain. The use of the two kinds of porcelain bulbs showed no perceptible difference. The oven for obtaining the high temperatures was electrically heated. In conclusion the authors show a comparison up to 1150° of the temperatures measured by the porcelain bulbs and platin-iridium bulb, which shows that the temperature for the former is systematically higher than for the latter, the difference increasing rapidly above 1000°. The reason given being that the porcelain bulbs develop a vapor at the high points. The authors intend to continue the work with the platin-iridium bulb for still higher temperatures.
H. T. B.

One-Component Systems

The allotropic modifications of phosphorus. *D. L. Chapman. Jour. Chem. Soc.* 75, *734* (*1899*). — Metallic and red phosphorus are identical. When red phosphorus is heated in a sealed capillary, it fuses at about the same temperature as potassium iodid.
W. D. B.

The thermal properties of isopentane. *S. Young. Zeit. phys. Chem.* 29, *193* (*1899*). — The object in view is an exact study of the relations of temperature, volume, and pressure throughout a wide range of temperature. Isopentane is well adapted for such study, being extremely stable, and easy to purify. Its boiling-point is 27.95°, the specific weight at 0° is 0.6393, the critical temperature 187.8°, pressure 25020 mm, volume 4.266 cc, whence the critical molecular volume is 306.5 cc. Determinations were made for the vapor-pressure at short intervals from −31.83° to the boiling-point and at somewhat wider intervals up to the critical temperature. Orthobaric volume curves are constructed throughout the range between 0° and the critical point, for the liquid, and from 10° to the same point, for the saturated vapor. A long list of measurements is given for the volume of 1 g substance as liquid and as unsaturated vapor under various pressures from ordinary temperatures up to the critical point and beyond this the change of volume of 1 g is traced as far as 280°. These results make possible the construction of a very complete series of isotherms, etc., throughout a wide range.

The exact determination of the critical volume not being possible, this value is obtained by extrapolation from the mean densities for liquid and vapor, which were determined up to 187.4° and give results agreeing very well with the formula

$$D = 0.3197 - 0.000454\,t.$$

The formula of van der Waals is inexact for volumes near and below the critical volume. For constant volume it may be thrown into the form

$$p = bT - a$$

$$\text{whence } \frac{dp}{dT} (= b) \text{ is constant.}$$

Applying this formula to the isochores deduced from the present results, it is found that there is a variation which is too regular to be attributable to experimental errors, and which leads to the conclusion reached by Amagat, that b is not absolutely constant. A comparison of the different critical relationships with those of benzene, shows that isopentane belongs in the same group with that substance, its halogen derivatives, ether, carbon tetrachlorid and stannic chlorid. *A. P. S.*

The vapor-pressures, specific volumes and critical constants of hexamethylene. *S. Young and E. C. Fortey. Jour. Chem. Soc.* 75, *873* (*1898*). — Pure hexamethylene melts at 4.7° and boils at 80.9°; its specific gravity at 0° is 0.79675. The critical data are: temperature, 280.0°; pressure, 30252 mm; density, 0.2733. In purifying hexamethylene the authors desired to freeze the impure liquid partially and then filter off the mother-liquor. This was done by having the platinum filter in the bottom of the tube covered by mercury until they were ready to begin filtering. *W. D. B.*

Note on NOCl and its compounds. *W. J. van Heteren. Zeit. anorg. Chem.* 22, *277* (*1899*). — Nitrosyl chlorid freezes at −65° and is miscible in all proportions with liquid chlorin. The compound $2SbCl_5.5NOCl$ melts at 180°; the compound $SnCl_4.2NOCl$ at 150°; and the compound $FeCl_3NOCl$ at 116°.

W. D. B.

A generally applicable process for determining vapor-densities under any pressure. *O. Bleier and L. Kohn. Monatsheft, 20, 505 (1899).* — A differential manometer is attached to a Victor Meyer tube and the change of pressure noted when the substance to be investigated is vaporized. From experiments with substances of known reacting weight, the authors determine the constant for the apparatus at that temperature, the increase in pressure due to one reacting weight. The merit of the apparatus consists in the fact that it is possible to work under diminished pressure just as readily as at atmospheric pressure.
W. D. B.

A method studying polymorphism and on polymorphism as the cause of some thermal peculiarities of chloral hydrate. *W. J. Pope. Jour. Chem. Soc. 75, 455 (1899).* — Berthelot found that the heat of fusion of recently solidified chloral hydrate was much less than that of chloral hydrate which had been solid for several days. Pope shows that the crystals which separate from the melt are not stable at ordinary temperatures. He speaks of the first form as stable at higher temperatures, which is a lax use of words, since there is nothing in the experiments to prove that the form which separates from the melt is stable at any temperature. *W. D. B.*

Nitro-camphor as an example of dynamic isomerism. *T. M. Lowry. Jour. Chem. Soc. 75, 211 (1899).* — The author shows that nitro-camphor and *p*-bromnitro-camphor exist in two liquid forms, the pseudo-compound being the more stable in each case. Equilibrium is reached in different lengths of time, depending upon the nature of the solvent. In all cases in which quantitative measurements of reaction velocity were made, it was found that the reaction was monomolecular and reversible. There is a very satisfactory discussion of the freezing-point and solubility relations for such systems, the only things overlooked by the author being the cryohydric point, the possibility of a reversal of stability at lower temperature and the effect of the initial temperature of heating. It is suggested that the multirotation of the sugars, or mutarotation as the author calls it, may be due to dynamic isomerism, to reversible equilibrium between two liquid forms. This is a very interesting paper, even though the theoretical treatment is not so novel as the author believes. *W. D. B.*

On the dissociation of gases at constant pressure. *R. Wegscheider. Monatsheft, 20, 307, 320 (1899).* — A discussion of the dissociation formulas when the concentrations are expressed in reacting weights of each component per sum of reacting weights, pressure, and temperature constant. The data of Würtz for phosphorus pentachlorid and of Friedel for methyl ether hydrochlorid are analyzed and recalculated. *W. D. B.*

Two-Component Systems

A new hydrate of potassium ferrous sulfate. *F. W. Küster and A. Thiel. Zeit. anorg. Chem. 21, 116 (1899).* — Solubility curves for three hydrates of potassium ferrous sulfate. The hydrate with six of water is stable below 30°; the one with four of water between 30° and 87°; the one with two of water above 87°. At 54° there is an instable inversion point with the hexahydrate and the dihydrate as solid phases. *W. D. B.*

The composition and tensions of dissociation of the ammoniacal chlorids of cadmium. *W. R. Lang and A. Rigaut. Jour. Chem. Soc.* 75, *833* (*1899*). — At 62° the dissociation pressure of $CdCl_2 6NH_3$ is 760 mm. The next lower compound is $CdCl_2 2NH_3$. *W. D. B.*

The volatility of osmium in a current of air or oxygen. *M. Vèzes. Zeit. anorg. Chem.* 20, *230* (*1899*). — It is pointed out that Sulc's observations (3, 247) are not new, having been made by Deville and Debray. Since the oxidizability of osmium varies with its previous history, no conclusions as to temperature limits are valid unless full details are given. *W. D. B.*

On chromic chlorid. *P. Rohland. Zeit. anorg. Chem.* 21, *37* (*1899*). — Violet chromic chlorid is practically insoluble in water and does not change over readily into the green form. Addition of very small quantities of chromous chlorid causes the change to take place rapidly, even in cold water.

W. D. B.

Definition and method of estimating the invasion and evasion coefficients for the solution of gases in liquids. *C. Bohr. Wied. Ann.* 68, *500* (*1899*). — The author extends the formula, which he had previously developed (2, 400), to express the relation between the absorption coefficient and temperature of a gas to higher points, and gives a careful experimental study of the absorption of CO_2 in water and sodium chlorid solutions between 0° and 60°. The evasion coefficient for the same gas from water and NaCl solutions is then treated, and his apparatus carefully described, involving many ingenious points. Simple straightforward formulæ are worked out connecting the different constants. *H. T. B.*

The melting of sodium thiosulfate; a contribution to our knowledge of hydrates. *F. W. Küster and A. Thiel. Zeit. anorg. Chem.* 21, *401* (*1899*). — Conductivity determinations of mixtures of sodium thiosulfate and water at 60° showed that there was no marked change when the solution had the formula $Na_2S_2O_3 5H_2O$. From this, the authors conclude that a certain amount of dissociation into the components takes place when hydrated sodium thiosulfate is melted. Unfortunately, the experiments give no clue as to the amount of dissociation. It would be very instructive if the authors would repeat their measurements with mixtures of acetic anhydrid and water, and with mixtures of copper and chlorin. *W. D. B.*

The relative efficiency and usefulness of various forms of still-heads for fractional distillation, with a description of some new forms possessing especial advantages. *S. Young. Jour. Chem. Soc.* 75, *679* (*1899*).—The author has made a quantitative study of the different forms of still-heads and of dephlegmator. The criteria for an ideal apparatus are: efficiency of separation; minimum amount of liquid left in apparatus; ease of construction and cheapness; freedom from liability to fracture; convenience in handling. To this list might well have been added: economy in the use of gas. The distillations were carried on at a constant rate, one drop per second, and the solution studied consisted of equal parts of benzene and toluene. Of the still-heads, the evaporator still-head designed by the author proved the most effective. In this apparatus, an inverted test-tube is placed over an inner tube through which the vapors ascend. The inverted test-tube is surrounded by the still-head proper and a little funnel is so suspended that the condensed liquids impinge on the top of the inverted test-tube. Of the dephlegmators, that devised by Young and Thomas proved the best.

The author explicitly rejected from consideration all still-heads kept at constant temperature and this seems to the reviewer a mistake. Theoretically we get absolute separation in one distillation with an apparatus of this type. It seems very probable that we should have seen better results if the same amount of ingenuity applied to developing a theoretically imperfect type had been utilized in attempts to make theory and practice coincide. *W. D. B.*

On a method for providing a current of gaseous chloroform mixed with air in any desired proportion and on methods for estimating the gaseous chloroform in the mixtures. *A. V. Harcourt. Jour. Chem. Soc. 75, 1060 (1899).* — An air current is passed slowly through a mixture of alcohol and chloroform and then through sulfuric acid to remove the alcohol. The author has determined the amount of chloroform in the vapor in equilibrium with known mixtures of alcohol and chloroform by adding water vapor to the chloroform and air, and then passing the mixed gases over a hot platinum wire. The chloroform is converted completely into hydrochloric acid. *W. D. B.*

A new inorganic dissociating medium. *P. Walden. Ber. chem. Ges. Berlin, 32, 2862 (1899).* — Liquid sulfur dioxid has the power of dissolving many substances in a marked degree. The characteristic colors of ions are pronounced and reactions take place with ease in this solvent. Conductivity results show that in some cases sulfur dioxid has a stronger ionizing tendency than water. Many of the iodids unite with sulfur dioxid to form complexes, as the boiling-point results show. A list of the substances which are soluble in the reagent is given, as are some of the conductivity results for some of the binary salts for different dilutions. Naphthalene, toluene, and acetanilid give normal results with the boiling-point method. Potassium, sodium, rubidium and ammonium iodids give nearly twice the normal molecular weight, while trimethyl sulfin iodid, tetra ethyl and tetra methyl ammonium iodids give approximately normal results.

No explanation is advanced to correlate the normal molecular weights obtained by the boiling-point method with the conductivity realized in the case of the iodids of the alkaline metals. *C. G. L. W.*

Characterization of racemic compounds. *F. S. Kipping and W. J. Pope. Jour. Chem. Soc. 75, 36 (1899).* — Experimental proof that a method for recognizing racemic compounds given by Ladenburg in 1894, is unsound. For Ladenburg's revised test see the succeeding review. *W. D. B.*

Contribution to the characterization of racemic compounds. *A. Ladenburg. Jour. Chem. Soc. 75, 465 (1899).* — "To characterize an inactive substance, that is, whether it is a racemic compound, or a mixture of its active components, determine the solubility of the substance without and with the addition of a small quantity of one or the other of its optically active components at the same temperature, and with the same solvent. If the solubilities are different, the substance in question is a racemic compound; if the same, it is an enantiomorphic mixture." *W. D. B.*

The characterization of "racemic" liquids. *F. S. Kipping and W. J. Pope. Jour. Chem. Soc.* 75, *1119* (*1899*). — It is pointed out that Ladenburg's general method for distinguishing racemic compounds (preceding review) is not new in its present form, and that Ladenburg evidently has not understood it because in practice he uses it to recognize racemic liquids, whereas the method applies only to solid compounds. *W. D. B.*

A method for discriminating between "non-racemic" and "racemic" liquids. *W. J. Pope and S. J. Peachey. Jour. Chem. Soc.* 75, *1111* (*1899*). — An optically active substance which shows polymerization by the Ramsay and Shields method is more likely to show a change of rotation constant with a change of solvent than a substance which is not so polymerized. This is confirmed by a study of the behavior of lævotetrahydroquinaldin and lævopinene. The authors then make what seems to them the probable assumption that when the solvent and solute are polymerized to the same degree, no change will take place on mixing. They confirm this view by an experiment with lævotetrahydroquinaldin in lævotetrahydroquinolin. They then show that the rotation constant of lævotetrahydroquinaldin when dissolved in the optically neutral mixture, is the same as when pure. From this they conclude that the optically neutral mixture of the two tetrahydroquinaldins is not a racemic liquid. Their experiment really shows nothing of the kind, though their conclusion is probably right in fact. *W. D. B.*

The influence of the solvent on the constitution of acetoacetic ester and similar compounds. *W. Wislicenus. Ber. chem. Ges. Berlin,* 32, *2837* (*1899*). — Weighed quantities of formyl phenyl acetic ester, formyl succinic ester, formyl malonic ester, and phenyl acetoacetic ester were dissolved in equal volumes of methyl alcohol, ethyl alcohol, ether, and benzene, and allowed to stand for some time, and after adding a drop of ferric chlorid solution the depth of color given in the different solvents was compared in a colorimeter. It was found that feebly dissociating media favor the maintenance of the enol form. The substances examined show a different behavior amongst themselves in the same solvent. Formyl succinic ester and formyl phenyl acetic ester show a marked tendency to tautomeric change. Acetoacetic ester on the other hand shows but little tendency to aldolization. *C. G. L. W.*

The changes of volume due to dilution of aqueous solutions. *E. B. H. Wade. Jour. Chem. Soc.* 75, *254* (*1899*). — An apparatus has been devised in which equal volumes of solution and solvent can be kept separated by a mercury column, measured, mixed, and remeasured. If the contraction be represented by X, the variation with the concentration is given by the formula:

$$X = n^b/a.$$

Here n is the volume concentration, b and a are constants. *W. D. B.*

The action of nitric oxide on nitrogen peroxide. *H. B. Dixon and J. D. Peterkin. Jour. Chem. Soc.* 75, *613* (*1899*). — When nitrogen peroxid is allowed to diffuse into nitrogen, carbonic acid or other indifferent gases, there is an increase of volume very nearly that required by the dissociation formula of Gibbs. When it is allowed to diffuse into nitric oxid, there is an infinitesimal decrease of volume. Since mixtures of nitric oxid with nitrogen or carbonic acid behave normally, it follows that some N_2O_3 is present in the mixtures of nitric oxid and nitrogen peroxid. *W. D. B.*

On the mode of burning of carbon. *H. B. Dixon. Jour. Chem. Soc.* 75, *630* (*1899*). — When oxygen, pure or diluted, is passed over coke heated to 500° some carbon monoxid is always formed, whether the gases are dried or not. On the other hand, carbon will not reduce dried carbonic acid at 500°. It seems necessary to conclude that carbon monoxid may result directly from the action of oxygen on carbon. This is in accord with the views of Brereton Baker, but contradicts the view of Lang. *W. D. B.*

The combustion of carbon disulphide. *H. B. Dixon and E. J. Russell. Jour. Chem. Soc.* 75, *600* (*1899*). —Carbon bisulfid has no sharp ignition point, a phosphorescent combustion occurring at low temperatures. When mixed with an insufficient quantity of oxygen and exploded, the products are carbon dioxid, carbon monoxid, sulfur dioxid, and carbonyl sulfid. Carbon bisulfid is not decomposed by heating to 400°. The detonation of mercury fulminate causes carbon bisulfid to dissociate into carbon and sulfur but only in the immediate neighborhood of the explosion. *W. D. B.*

Estimation of boric acid mainly by physical processes. *A. W. Blyth. Jour. Chem. Soc.* 75, *722* (*1899*). — The unknown amount of boric acid dissolved in methyl alcohol is added to three grams of ordinary dextrotartaric acid and the solution made up to 20 cc by addition of methyl alcohol. The optical activity is measured and the amount of boric acid read off from the previously prepared table.

Boric acid can also be determined by boiling with a sodium carbonate solution and measuring either the amount of carbon dioxid given off or the change in conductivity. *W. D. B.*

Poly-Component Systems

Equilibrium phenomena between manganous hydroxid and ammonium salts. *W. Hertz. Zeit. anorg. Chem.* 21, *243* ; 22, *279* (*1899*). — When ammonium chlorid, ammonium nitrate, or ammonium sulfate solutions of varying concentrations are added to solid manganous hydroxid, the amount of manganese going into solution is a function of the concentration of the ammonium salt. For the chlorid, the reaction may be written

$$MnO_2H_2 + 2NH_4Cl \rightleftharpoons MnCl_2 + 2NH_4OH.$$

As long as the ammonium salts were not present in too dilute solution, the ratio between the manganese and the ammonium salts was constant instead of having the calculated exponent. In the second paper it is suggested that this discrepancy may be due to neglecting the incomplete dissociation of the manganous salt. When very dilute solutions of the ammonium salts are taken, the results agree better with the theoretical values. *W. D. B.*

The decomposition of certain racemic amido-acids into their active components. *E. Fischer. Ber. chem. Ges. Berlin,* 32, *2451* (*1899*). — Inactive alanin is benzoylated by a modified Schotten-Baumann method and the benzoyl derivative combined with brucin. The *l*-modification precipitates on standing as long plates. The benzoyl compound is decomposed with hydrochloric acid. The specific rotation of *l*-alanin $= [\alpha]_D^{20} = -9.68$. Racemic asparaginic acid was treated similarly and gave *l*-asparaginic acid. Rotation $= [\alpha]_D^{20} = -9.04$. The *l*-glutaminic acid prepared in the same way shows a rotation in the form of its hydrochlorid of $[\alpha]_D^{20} = -30.05$. *C. G. L. W.*

The application of powerful optically active acids to the resolution of externally compensated basic substances. Resolution of tetrahydroquinaldine. *W. J. Pope and S. J. Peachey. Jour. Chem. Soc.* 75, *1066* (*1899*). — An optically neutral mixture of two optically active bases can often be resolved by adding an optically active acid, the resulting salts often having different solubilities. The authors have had the ingenious idea of adding a mixture consisting of an optically active acid and an approximately equally dissociated but optically inactive acid, the separation being thus much more complete. By adding dextro-α-bromo camphor sulfonic acid and hydrochloric acid to an optically neutral mixture of the two tetrahydroquinaldins, pure samples of lævotetrahydroquinaldin dextro-α bromo camphor sulfonate were obtained. The dextro compound could not be obtained pure from the residues because two solid phases separated, the racemic compound and the dextro-salt. It did not occur to the authors to try fractional crystallization at different temperatures, in which case they could probably have effected a separation. *W. D. B.*

Resolution of tetrahydroparatoluquinaldin. *W. J. Pope and E. M. Rich. Jour. Chem. Soc.* 75, *1093* (*1899*). — Further applications of Pope's new method (preceding review). *W. D. B.*

Resolution of camphoroxime. *W. J. Pope. Jour. Chem. Soc.* 75, *1105* (*1899*). — Further applications of Pope's new method (two reviews back). *W. D. B.*

Action of light and of oxygen on dibenzyl ketone. *E. C. Fortey. Jour. Chem. Soc.* 75, *871* (*1899*). — Dibenzyl ketone that had stood for five years in stoppered bottles exposed to the light was found to have decomposed to a certain extent, benzaldehyde, benzoic acid, and phenylacetic acid being formed. A sealed tube containing pure dibenzyl ketone and oxygen was heated in the dark to 100° for ten days and gave an acid reaction when opened, while a tube containing only dibenzyl ketone remained unchanged, even in the vapor of boiling quinolin. Absence of moisture does not prevent the decomposition, which is evidently due to air and is accelerated by light and heat. If, however, dibenzyl ketone by itself or in presence of carbon dioxid be exposed to light for several years, a decomposition takes place into carbon monoxid and a condensation product. *W. D. B.*

The aluminum-mercury couple, I. *J. B. Cohen and F. W. Skirrow. Jour. Chem. Soc.* 75, *887* (*1899*). — Sulfur chlorid S_2Cl_2 reacts energetically with hydrocarbons in presence of small quantities of the aluminum-mercury couple.
W. D. B.

The aluminum-mercury couple, II. *J. B. Cohen and H. B. Dakin. Jour. Chem. Soc.* 75, *893* (*1899*). — Bromin reacts energetically with hydrocarbons in presence of small quantities of the aluminum-mercury couple. *W. D. B.*

The oxidation of polyhydric alcohols in presence of iron. *J. H. Fenton and H. Jackson. Jaur. Chem. Soc.* 75, *1* (*1899*). — Polyhydric alcohols are readily oxidized by hydrogen dioxid in presence of ferrous iron while practically no reaction takes place when there is no iron. Glycol, glycerol, and erythritol are oxidized in the sunlight by atmospheric oxygen when ferrous iron is present.
W. D. B.

On the determination of sulfuric acid in presence of iron. *F. W. Küster and A. Thiel. Zeit. anorg. Chem.* 21, *73* (*1899*). — Rejoinder to Lunge (3, 251).
W. D. B.

On the determination of sulfuric acid in presence of iron. *G. Lunge. Zeit. anorg. Chem.* 21, *194* (*1899*). — Counter-rejoinder to Küster and Thiel (preceding review.) *W. D. B.*

The determination of sulfur in pyrites in presence of iron. *O. N. Heidenreich. Zeit. anorg. Chem.* 20, *233* (*1899*). — Following out the idea suggested by Küster and Thiel (3, 251) the author reduces the ferric sulfate to ferrous sulfate by means of metallic zinc before precipitating barium sulfate. *W. D. B.*

On the absorption of nitrogen. *W. Hempel. Zeit. anorg. Chem.* 21, *19* (*1899*). — A mixture of one gram powdered magnesium with five grams granulated calcium oxid and 0.25 g sodium in small pieces absorbs nitrogen much more rapidly than other mixtures tested by the author, while calcium oxid and sodium without the magnesium do not absorb nitrogen at all.
W. D. B.

Standardizing in iodometry. *J. Wagner. Zeit. anorg. Chem.* 19, *427* (*1899*). — Reviewed (3, 48) from the author's *Habilitationsschrift.*

The preparation of cesium from its carbonate. *E. Graefe and M. Eckardt. Zeit. anorg. Chem.* 22, *158* (*1899*). — Cesium can easily be prepared in quantity by heating the carbonate with magnesium powder in an iron tube through which a current of hydrogen passes. Cesium is more readily reduced in this way than rubidium or potassium. *W. D. B.*

Velocities

The decomposition of ferric acetate. *W. Herz. Zeit. anorg. Chem.* 20, *16* (*1899*). — Ferric acetate reacts with water to form a basic salt and acetic acid. Since the reaction does not run to an end, and since the acetic acid has an accelerating effect, the ordinary formula for a monomolecular reaction holds only for short periods of time. *W. D. B.*

Esterification constants of substituted acetic acids. *J. J. Sudborough and L. L. Lloyd. Jour. Chem. Soc.* 75, *467* (*1899*). — The authors have studied the rate at which substituted acetic acids are converted into esters when dissolved in ethyl alcohol, *n*/40 HCl being used as catalytic agent. Acetic acid gave the highest reaction velocity while mono-substituted acids react more rapidly than di-substituted acids, and these latter than tri-substituted acids. This order is entirely different from that obtained in experiments involving autocatalysis only. *W. D. B.*

On electrolytic reaction velocity. *E. Cohen. Zeit. Elektrochemie*, 6, *85* (*1899*). — Reviewed (3, 425) from Proc. Roy. Acad. Amst. 1899, 334.

A new method of separating racemic compounds into their active components. *W. Marckwald and A. McKenzie. Ber. chem. Ges. Berlin*, 32, *2131* (*1899*). — The methods which have been used so far to separate racemic compounds into their active components are, the separation of enantiomorphous crystals mechanically, the use of bacteriological methods, and the combination of active acids and bases with inactive bases and acids. The authors have proposed to use the difference in the velocity of esterification with an active alcohol as a means of separating two acids such as *d*- and *l*-mandelic acid. The alcohol used was menthol. The *d*-mandelic acid forms an ester more rapidly than does its optical antimer. On heating a mixture of menthol with racemic mandelic acid, the acid unused in the formation of the ester shows a lævorotatory power. This acid was fractionally crystallized and converted into its magnesium and cadmium salts. By a series of crystallizations of the salts it was possible to obtain a small quantity of *l*-mandelic acid. The impure menthyl *d*-mandelate was fractionally saponified and a quantity of pure *d*-mandelic acid was obtained. The amounts of the active acids recovered was not sufficient to warrant the use of the method in its present state for the preparation of the optically active acids from synthetic mandelic acid. *C. G. L. W.*

The hydration of calcium oxid. *P. Rohland. Zeit. anorg. Chem.* 21, *28* (*1899*). — The time in which a given quantity of calcium oxid becomes hydrated, when in presence of an excess of water, varies with the nature of the substances dissolved in the water. Calcium chlorid and aluminum chlorid increase the reaction velocity very much, barium chlorid slightly, potassium and sodium chlorids not at all. Calcium chromate and potassium bichromate retard the reaction. The strong acids and also acetic acid have an accelerating effect, the hydroxids of the alkalies a retarding effect, and calcium hydroxid is indifferent. Organic compounds with two or more hydroxyl groups retard the reaction; others accelerate it. *W. D. B.*

Electromotive Forces

On the electromotive behavior of chromium, II. *W. Hittorf. Zeit. Elektrochemie*, 6, *6*; *Zeit. phys. Chem.* 30, *481* (*1899*). — Experiments to confirm the author's belief (2, 450) that the passive state of chromium is not due to a film of oxid. Active chromium is rapidly attacked at high temperatures, slowly at low temperatures by dilute hydrochloric acid, with formation of $CrCl_2$. If it is made anode and a heavy current passed, it becomes passive and chromic acid is formed. On making it cathode, it becomes active again. In dilute hydriodic acid, active chromium dissolves with formation of CrI_2; when anode in the same solution, iodin is set free. When chromium is oxidized on the surface by heating in air and is then put in the cell Cr | NaCl | H_2CrO_4 | Pt it dissolves readily with formation of $CrCl_3$. *W. D. B.*

The electromotive activity of carbon monoxid. *V. Hoeper. Zeit. anorg. Chem.* 20, *419* (*1899*).—The cell Pt_{CO} | *n*HCl | KClHgCl | Hg has an electromotive force of 0.10 to 0.15 volts, mercury being anode. Substituting pure oxygen for carbon monoxid raised the value to 0.55, while a mixture of air and oxygen gave 0.43 and a mixture of carbon monoxid and air 0.15-0.18. Replacing the platinum electrodes by carbon made no real difference in the electromotive force though it then took very much longer to reach equilibrium. It was found that the potential difference, platinum and carbon monoxid in cuprous chlorid and hydrochloric acid differed but slightly from that of platinum without carbon monoxid in cuprous chlorid and hydrochloric acid, a fact which is interesting in its bearing on the Borchers gas cell. *W. D. B.*

On the change of the free energy in the fused halid compounds of some metals. *O. H. Weber. Zeit. anorg. Chem.* 21, *305* (*1899*).—The author has repeated and extended the work of Czepinski (3, 255). By using porcelain vessels, it was possible to make measurements up to 1000° in some cases. By separating the anode chamber from the cathode chamber, it was possible to eliminate some of the irregularities observed by Czepinski, which were due to the depolarizing effect of the vapor from the metallic regulus.

The change of the electromotive force with the temperature is very nearly constant, showing that the heat of reaction is practically independent of the temperature. This is not true, however, for cadmium chlorid cells at temperatures above the boiling-point of cadmium. The difference between the electromotive forces of the cells Pb | $PbCl_2$ | KCl, NaCl | AgCl | Ag and Pb | $PbBr_2$ | KCl, NaCl | AgBr | Ag is practically independent of the temperature, the electromotive force of the first cell being about 0.07 volt higher than that of the other.

W. D. B.

On the change of the free energy in the fused halid compounds of some metals. *R. Lorenz. Zeit. anorg. Chem.* 22, *241* (*1899*).—A general discussion of the results obtained by Weber (preceding review). Bodländer had calculated 1.59 volts as the decomposition voltage of solid lead chlorid, this result being based on the solubility of this salt in water. Extrapolating from Weber's data Lorenz calculates a value less than 1.65 volts, agreeing very well with the conclusions of Bodländer. *W. D. B.*

On the theory of the lead accumulator. *K. Elbs. Zeit. Elektrochemie*, 6, *46* (*1899*).—The author gives his reasons for believing that we have to deal with tetravalent lead and not with the anion PbO_2. In the discussion that followed, Ostwald advanced the view that everything which may take place does take place. In consequence all theories are right. This rather depressing view met with general approbation, Nernst alone raising his voice against it.

W. D. B.

Studies on the lead accumulator. *M. Mugden. Zeit. Elektrochemie,* 6, *309* (*1899*). — It is shown that lead sulfate is formed primarily when the lead accumulator is discharged. There is also a discussion of the lead sulfate, sulfuric acid concentration cell. *W. D. B.*

Contributions to the theory of the lead accumulator. *F. Dolezalek. Zeit. Elektrochemie,* 5, *533* (*1899*). — The author shows that for concentrations between double and hundredth normal, the formula for the accumulator may be written

$$E_c = 1.895 + 0.120 \log_{10} C + 0.001\ C.$$

The author calculates the dissociation of pure water at 0° as 0.33×10^{-7} while Kohlrausch and Heydweiller made it 0.35×10^{-7}. Determinations of the single potentials by means of the hydrogen and the mercurous sulfate electrode showed that the tendency to self-discharge increases with increasing concentration of the acid. *W. D. B.*

Determination of electromotive force, and of conductivity as an aid in preparing saturated solutions. *J. H. van 't Hoff. Zeit. Elektrochemie,* 6, *57* (*1899*). — Equilibrium in polycomponent systems is often reached so slowly that it becomes essential to have some means of determining when there is no further change. In such systems solubility determinations are unsatisfactory for this purpose, owing to the difficulty of making them and to the consequent change in the composition of the system. The author has therefore made conductivity measurements to determine when no further change takes place, but finds that measurements of electromotive force are more satisfactory for this purpose. A description of the preliminary apparatus is given. *W. D. B.*

Electroaffinity, a new factor in chemical classification. *R. Abegg and G. Bodländer. Zeit. anorg. Chem.* 20, *453* (*1899*). — In organic compounds we have to consider only the affinity of the constituents for each other, while in inorganic compounds we have also to consider the affinity for electricity or the tendency to form ions, the term log P of the Nernst formula. One would expect that the solubility of a salt would vary directly with the solution pressures of the ions. This is approximately true for sparingly soluble salts, but not for those which are very soluble. The degree of dissociation in aqueous solutions is then discussed with reference to the free energy of the solid, the solubility of the undissociated salt, and the electro-affinity. The greater the electro-affinity of two salts, the less will be the tendency to form complex salts. [This would seem to imply that complex salts would be formed less readily in water than in other solvents.]

Since we have complex anions there is no reason why we should not have complex cations, and such a one occurs in the salt $[Ag_3I](NO_3)_2$ in which the iodin is part of the cation. The authors look upon chloric and perchloric acids as molecular compounds of oxygen with chlorin analogous to hydrates. The fact that chlorin, bromin, and iodin as ion have practically the same migration velocity is attributed by the authors to the existence of hydrated ions. The whole discussion is necessarily vague and not very accurate, but on the other hand it is very interesting, and the views put forward by the authors may well form a useful working hypothesis which will lead to the discovery of many important facts. *W. D. B.*

The measure of the electric constants. *K. Schreber. Wied. Ann.* **68**, *607* (*1899*). — The author considers the fundamental units in electricity should be the ohm, volt and ampere, and devotes the entire paper in endeavoring to show the impossibility of referring them to the units of length, time and mass without introducing ambiguity and absurd mathematical reasoning. *H. T. B.*

A quantitative electrolytic separation of the halogens, chlorin, bromin, iodin. *H. Specketer. Zeit. anorg. Chem.* **21**, *273* (*1899*). — Reviewed (3, 65) from the preliminary paper, Zeit. Elektrochemie, **4**, 539 (1898).

Electrolysis and Electrolytic Dissociation

The theory of the electrolytic formation of hypochlorite and chlorate. *F. Foerster. Zeit. Elektrochemie*, **6**, *11*; *Zeit. anorg. Chem.* **22**, *1* (*1899*). — For neutral and slightly acid solutions the author makes the two assumptions that chlorin is continually set free at the anode and that the hypochlorite as ion is also discharged at the anode with evolution of oxygen. The formation of chlorate thus becomes a secondary process with hypochlorite as an intermediate stage. Decreasing current density at the anode therefore increases the formation of chlorate; rise of temperature increases the rate at which hypochlorite changes into chlorate and the amount of chlorate relatively to hypochlorite; free acid has the same effect coupled with the disadvantage of a slight evolution of chlorin so that the solution gradually becomes neutral. In markedly alkaline solutions, it is necessary to adopt Oettel's assumption of a primary formation of chlorate. *W. D. B.*

Experimental investigation on the formation of hypochlorite and chlorate by the electrolysis of alkaline chlorids. *E. Müller. Zeit. anorg. Chem.* **22**, *33* (*1899*). — An investigation undertaken to test the theory of Foerster (preceding review). The final conclusion is that the formation of chlorate may be due to any one of the following four reactions:

$$(1)\ \overset{-}{\mathrm{Cl}} + 3\mathrm{HClO} = \overset{-}{\mathrm{ClO_3}} + 3\overset{+}{\mathrm{H}} + 3\overset{-}{\mathrm{Cl}}.$$

$$(2)\ \overset{-}{\mathrm{ClO}} + 2\mathrm{HClO} = \overset{-}{\mathrm{ClO_3}} + 2\overset{+}{\mathrm{H}} + 2\overset{-}{\mathrm{Cl}}.$$

$$(3)\ \overset{-}{\mathrm{Cl}} + 3\mathrm{O} = \overset{-}{\mathrm{ClO_3}}.$$

$$(4)\ \overset{-}{\mathrm{ClO}} + 2\mathrm{O} = \overset{-}{\mathrm{ClO_3}}.$$

In dilute hydrochloric acid solution the reaction takes place exclusively according to (3); in all other cases, according to all four equations, though in varying relative amounts. In slightly acid, neutral, or slightly alkaline solutions where there is no great tendency to evolution of oxygen, equations (1) and (2) represent the important changes. In markedly alkaline solutions reactions (3) and (4) are the prominent ones.

Several interesting points were brought out in the course of the experiments. When the anode was kept very cold, crystals of chlorin hydrate were obtained.

On electrolyzing a solution of nearly pure NaClO it was found that ninety percent of the change to chlorate was due to a secondary reaction and not to oxidation by oxygen. Carbonic acid causes rapid change of hypochlorite into chlorate and by passing carbonic acid into a potassium chlorid solution containing chromate an electrolytic efficiency of seventy-one percent was obtained. Platinizing the anode cuts the yield down enormously, in one set of measurements from 43.5 to 3.1 percent. In converting potassium chlorate into perchlorate, a similar phenomenon was observed, the yield dropping from ninety-five to nineteen percent. *W. D. B.*

Remarks on the address of Prof. Foerster: "On the reactions during the electrolysis of alkaline chlorid solutions". *H. Wohlwill. Zeit. Elektrochemie, 6, 227 (1899).* — A criticism of Foerster's view (two reviews back) that the formation of chlorate is due to the oxidation of ClO as ion by hypochlorous acid. *W. D. B.*

Reply to the comments of H. Wohlwill. *F. Foerster. Zeit. Elektrochemie, 6, 253 (1899).* — It is claimed that Wohlwill's reasoning (preceding review) is based on a series of unproved assumptions. *W. D. B.*

An electrolytic process for making the chlorates, bromates, and iodates of the alkalies. *E. Müller. Zeit. Elektrochemie, 5, 469 (1899).* — Addition of less than two grams of potassium chromate to a liter of potassium chlorid solution causes the efficiency to rise to about seventy percent, owing to the decreased reduction at the cathode. On making the same addition to a potassium bromid solution it became possible to convert 97.6 percent of this salt into bromate with an average electrical efficiency of 94 percent. Under the same conditions, 97.7 percent of the total potassium iodid was converted into iodate with an average electrical efficiency of 97 percent. When reduction at the cathode is to be avoided, platinum or nickel is the best electrode, though iron and copper are nearly as good. Lead as cathode increases the amount of reduction very much, and zinc is twice as bad as lead. *W. D. B.*

The electrolytic synthesis of mixed azo-compounds. *W. Löb. Zeit. Elektrochemie, 5, 450 (1899).* — Starting with mixtures of nitro-compounds, the author has been able to prepare mixed azo-compounds by electrolytic reduction. The conditions are given for making seven of these substances. Platinum or nickel electrodes may be used but the reduction goes too far with lead electrodes. The reaction does not take place with the nitrophenols. *W. D. B.*

An electrolytic modification of the methods of Sandmeyer and Gatterman. *E. Volocek and E. Zenisek. Zeit. Elektrochemie, 5, 485 (1899).* — A solution containing cupric chlorid and the diazo compound is electrolyzed between copper electrodes. The yield is better than in the regular reaction. In the one case in which bromin was substituted for the amido group, the yield was not very satisfactory, but this was probably due to the fact that only the theoretical amount of bromid was taken instead of a large excess. *W. D. B.*

Electrolysis of benzoic acid. *C. Schall. Zeit. Elektrochemie, 6, 102 (1899).* — On passing a hundred-volt current through a solution of sodium benzoate in fused benzoic acid, the author obtained small quantities of diphenyl. *W. D. B.*

On the appearance of carbylamin during the electrolysis of alcoholic, alkaline solutions of nitrobenzene and anilin without a diaphragm. *J. Möller. Zeit. Elektrochemie*, 5, *463* (*1899*). — After a hot solution containing nitrobenzene, sodium hydroxid, water and alcohol had been electrolyzed for thirty-six hours between platinum electrodes, there was noticed the characteristic isonitrile odor. Unsuccessful attempts were made to isolate carbylamin. *W. D. B.*

On manganese cesium alum. *A. Piccini. Zeit. anorg. Chem.* 20, *12* (*1899*). — When manganese sulfate and cesium sulfate are dissolved in aqueous sulfuric acid and electrolyzed with a platinum anode, a manganese cesium alum is obtained provided the solution be stirred thoroughly and kept below 15°. [Cf. 3, 518]. *W. D. B.*

Observations on the phenomena occurring in the electrolysis of copper sulfate solutions. *F. Foerster. Zeit. Elektrochemie*, 5, *508* (*1899*). — Mechanical tests show that copper precipitated at 40° is much tougher than copper precipitated at 20° or at 60°; but it is inferior to worked copper. Presence of sodium sulfate lowers the temperature at which the toughest copper is precipitated. If India rubber or other organic substances come in contact with the cathode solution, a very brittle copper is obtained. When using impure copper as anode, more of the impurities remain as anode mud with a high than with a low current density. At 70° the amount of mud increases enormously, but is largely composed of crystallized copper, presumably due to the decomposition of cuprous sulfate. *W. D. B.*

Further contributions to our knowledge of the nature of zinc mud. *F. Foerster and O. Günther. Zeit. Elektrochemie*, 6, *301* (*1899*). — A natural consequence of the theory of the authors (3, 64) is that zinc should precipitate in a firm coherent mass from sodium zincate solution. This is not the case and the authors find themselves reduced to the assumption that hydroxyl as ion has a disturbing effect. Incidentally they have prepared solid sodium zincate, having the formula $ZnONaOH3H_2O$. They also call attention to the fact that zinc precipitates nicely from a five percent zinc chlorid solution to which a slight excess of ammonia is added, while it separates in large crystals from a solution containing one-half of one percent of zinc and ammonia in excess.

W. D. B.

On the electrolysis of fused zinc chlorid. *H. S. Schultze. Zeit. anorg. Chem.* 20, *323* (*1899*). — Lorenz noticed that so-called pure zinc chlorid when fused and electrolyzed gave off hydrogen for a time. This has been confirmed by the author who finds that a bluish-gray powder is also formed. The evolution of hydrogen and the formation of the powder can also be brought about by the addition of metallic zinc. The cause of the trouble is water, and the powder is apparently an oxid of zinc. So-called pure zinc chlorid contains either water or hydrochloric acid. If the latter, it can be electrolyzed at once with precipitation of zinc. *W. D. B.*

Electrolytic separation of low-grade coin silver. *A. Dietzel. Zeit. Elektrochemie*, 6, *81* (*1899*). — The author discusses the methods of obtaining gold, silver, and copper from an alloy containing 5.7 pct gold, 22.50 pct silver, 40.65 pct copper, and small quantities of other metals. The alloy is made anode in an acid copper nitrate solution, the gold remaining undissolved. The silver is precipitated by metallic copper outside the electrolytic cell and the copper is obtained by electrolysis. *W. D. B.*

Observations on the electrolysis of cane-sugar solutions. *K. Ulsch. Zeit. Elektrochemie,* 5, *539* (*1899*).—The object was to oxidize sugar completely to carbon dioxid. In sulfuric acid solutions the most effective oxidation is obtained when the liquid is kept cool, while a hot solution is more effective when the electrolyte is barium or potassium hydroxid. In no case is the oxidation complete. If the barium hydroxid solution be treated with permanganate, values are obtained identical with those from combustions; but this is not true with the sulfuric acid or the potassium hydroxid solutions. *W. D. B.*

On the process at the aluminum anode. *K. Norden. Zeit. Elektrochemie,* 6, *159, 188* (*1899*).—After a very lengthy critical sketch of the subject, the author describes his own experiments. By reversing the current occasionally, it was possible to detach the film mechanically from the anode and to get eventually enough of it on the bottom of the vessel for an analysis. Since a certain amount of aluminum dissolves, apart from the action of the current, many factors have to be taken into account. The final conclusion is that the film is aluminum hydroxid. *W. D. B.*

On the electrolysis of the alkaline earths. *J. Sarghel. Zeit. Elektrochemie,* 6, *149, 173* (*1899*).—High temperature, provided it is not too high, and high current density at the cathode increase the yield of calcium bromate from calcium bromid. A rough cathode is also essential since the protecting diaphragm of calcium hydroxid falls off readily from a smooth electrode. The yield from magnesium bromid is less than from calcium bromid because magnesium hydroxid is too insoluble. *W. D. B.*

On the reducing action of electrolytically precipitated metals. *A. Binz and A. Hagenbach. Zeit. Elektrochemie,* 6, *261* (*1899*).—Experiments showing that while dye-stuffs are usually reduced by electrolytic hydrogen, they are more readily reduced by electrolytic sodium, potassium, or zinc. *W. D. B.*

The blue salt of Fehling's solution and other cuprotartrates. *O. Masson and B. O. Steele. Jour. Chem. Soc.* 75, *725* (*1899*).—Caustic potash solution was added to pure cupric tartrate until the solid was nearly all dissolved. The resulting solution was neutral to litmus. It was placed in a tube, the two ends of which were stopped by plugs of sodium chlorid in a gelatine jelly. On passing the electric current, the blue color moved to the anode. The blue anions are not the only ones. In an experiment with cupric sulfate, sodium chlorid jelly, and neutral Fehling's solution, the light blue copper ions moved to the right, the dark blue ions to the left, but a bluish precipitate, presumably of copper tartrate, was formed before the two boundaries came together. Synthetic experiments showed that the formation of the neutral Fehling's solution may probably be expressed by the equation:

$$5NaOH + 4CuC_4H_4O_6 = Na_2C_4H_4O_6 + Na_3C_{12}H_7Cu_4O_{18} + 5H_2O.$$

W. D. B.

Is finely powdered or coarse ground material preferable for making calcium carbid? *B. Carlson. Zeit. Elektrochemie*, 6, *324* (*1899*). — Reasons are given why a powdered meal should not be used for making calcium carbid.
W. D. B.

On a new fluid interrupter. *H T. Simon. Wied. Ann.* 68, *860* (*1899*). — It would have been more to the point if the author had given Wehnelt a little more credit for the essential idea of his so-called new fluid interrupter, and instead of claiming the credit of a discovery had been content to call it, as it is, a modification of the Wehnelt break. The modification was described previously by Wehnelt (see review) and consists in replacing the small platinum point forming the "active" electrode by a small hole in a glass vessel separating two electrodes. The best Simon modification is where the electrodes are separated by a glass plate in which a number of small 1 mm holes are made which can be so multiplied as to limit the speed of interruption. Another modification is to connect two fluid cells by a small glass U-tube. The former is undoubtedly the most useful interrupter for an induction coil that has yet been devised.
H. T. B.

The internal resistance of normal elements. *E. Cohen. Zeit. phys. Chem.* 28, *723* (*1899*). — The internal resistance of the Clark and Weston cells varies irregularly with the amount of crystals present. In cells without crystals, the resistance is proportional to the resistance of the solutions. *W. D. B.*

On the conductivity of fused zinc chlorid. *H. S. Schultze. Zeit. anorg. Chem.* 20, *333* (*1899*). — Expressed in reciprocal ohms and referred to a centimeter cube, the conductivity of zinc chlorid is 0.460 at 700°; 0.104 at 500°; 0.00186 at 300°; 0.00011 at 260°. The author makes the melting-point about 290°-300°, some thirty degrees higher than the figures of Braun and Graetz.
W. D. B.

Determining the saturation of solutions by measuring the conductivity. *H. M. Dawson and P. Williams. Zeit. Elektrochemie*, 6, *141* (*1899*). — By fastening the electrodes into the glass, the authors have made a piece of apparatus in which there is no danger of evaporation. When the specific conductivities of saturated sodium sulfate solutions are plotted against temperatures, the resulting curve shows a break at 32.55°; but, owing to the great solubility of sodium sulfate, this is not very marked. With saturated solutions of thorium sulfate, a very marked break was obtained at 48°. This being five degrees higher than the inversion temperature originally found by Roozeboom, further measurements were made with the tensimeter and the dilatometer. With the latter instrument a reading of 46.5° was obtained, while the inversion temperature was between 47° and 48° according to the tensimeter. *W. D. B.*

Electrolytic conductivity of solids at very high temperatures. *W. Nernst. Zeit. Elektrochemie*, 6, *41* (*1899*). — Mixed oxids of the rare earths conduct better at very high temperatures than sulfuric acid at 18°. The conduction is electrolytic, but there are only the merest traces of decomposition, this being a case where the 'residual' current is the main phenomenon. *W. D. B.*

On the electrolytic properties of platinum and tin chlorids. *W. Dillenberger and R. Dietz. Wied. Ann.* 68, *853* (*1899*). — The authors find that the conductivity of a platinum chloride solution increases with time and show it is due to the formation of hydrochlorplatinic acid thus:

$$2H_2PtCl_4O = H_2PtCl_6 + PtCl_2O + H_2O.$$

The results agree with those of Hittorf in making the transition number of the anion decrease with the concentration. The authors assume the tin chlorid to split into the ions Sn and Cl_4. They consider the small appearance of the tin on the cathode to be conditioned by a secondary process, and is not easily shown owing to the great difference in the migration power of the Sn and Cl.

H. T. B.

A new substance with high resistance. *W. C. Heraeus. Zeit. Elektrochemie*, 6, *43* (*1899*). — When a mixture of earthenware and platinum is heated almost to melting, a change takes place and the substance becomes a conductor with a very high resistance. It is probable that there is formed a compound of platinum and silicon. *W. D. B.*

The present status of technical electrochemistry. *W. Borchers. Zeit. Elektrochemie*, 6, *61* (*1899*). — Lists are given of the elements prepared wholly or in part by electrical means; of the number of horse-power soon to be available in different countries for electrochemical purposes; of the amount and estimated value of the possible annual output in different parts of the world of a dozen or more of the most important electrochemical products. *W. D. B.*

Experiments with carbon electrodes. *J. Zellner. Zeit. Elektrochemie*, 5, *450* (*1899*). — The less porous carbon is, the better it is, as a rule, for electrolytic purposes. Though this test is not absolute, it is more reliable than an estimate based on the density. Carbon electrodes last longest in neutral or alkaline electrolytes. The evolution of oxygen in acid solutions is particularly destructive while chlorin has much less effect. In the same electrolyte the consumption of carbon is roughly proportional to the current density. *W. D. B.*

Universal electrolytic stand. *F. Peters. Zeit. Elektrochemie*, 6, *277* (*1899*). — A stand which will not tip over, which can be raised or lowered, and which does not involve loose-flying wires. It is sold by Kaehler and Martini.

W. D. B.

Dielectricity and Optics

The decomposition of racemic mandelic acid and its properties. *E. Rimbach. Ber. chem. Ges. Berlin*, 32, *2385* (*1899*). — Inactive mandelic acid was separated by means of cinchonin. The exact methods of obtaining the crystalline salt are given. The addition of sodium chlorid solution favors the precipitation of cinchonin *d*-mandelate. Crystallographic measurements of *d*-mandelic acid are given. The rotation of the acid is $[\alpha]_D^{20^\circ} = + 212.52 - 0.5777\,q$; $q =$ 91 — 87 according to the interpolation formula. The rotation dispersion is fairly strong. The melting-point of the inactive acid is lower than that of the active acids. (118° and 134°). The inactive acid is not a mixture but a true racemic compound. *C. G. L. W.*

A study of the absorption spectra of isatin, carbostyril, and their alkyl derivatives in relation to tautomerism. *W. N. Hartley and J. J. Dobbie. Jour. Chem. Soc.* 75, *640* (*1899*). — The absorption spectra were determined photographically, cadmium electrodes being used as the source of light. Methyl and ethyl pseudocarbostyril are true alkyl derivatives from carbostyril, while methyl carbostyril is not. Isatin and methyl pseudo-isatin evidently are of similar constitution, while methyl isatin must be quite different. *W. D. B.*

Position isomerism and optical activity; the methylic and ethylic salts of benzoyl and of ortho-, meta-, and para-malic acid. *P. Frankland and F. M. Wharton. Jour. Chem. Soc.* 75, *337* (*1899*). — Determinations of the rotation of the plane of polarized light. *W. D. B.*

Some regularities in the rotary power of homologous series of optically active compounds. *P. Frankland. Jour. Chem. Soc.* 75, *347* (*1899*). — Discussion of the preceding paper. *W. D. B.*

The rotatory power of optically active methoxy- and ethoxy-propionic acids prepared from active lactic acid. *T. Purdie and J. C. Irvine. Jour. Chem. Soc.* 75, *483* (*1899*). — Determinations of the rotation of the plane of polarized light. *W. D. B.*

The comparative rotatory powers of methylic and ethylic ditoluyl glycerates. *P. Frankland and H. Aston. Jour. Chem. Soc.* 75, *493* (*1899*). — Determinations of the rotation of the plane of polarized light. *W. D. B.*

The blue steam ray. *A. Bock. Wied. Ann.* **68**, *675* (*1899*). — The author studies the effect of concentrated HCl on a steam jet and shows photometrically that the blue color given to the jet is the same as the blue of the heavens. He also studies the polarization effect for different colored lights and finds that red, yellow and green are polarized by the jet, while blue and violet are not. By defraction the size of the drops in the jet are given as 0.0009 mm. *H. T. B.*

Crystallography, Capillarity, and Viscosity

On the surface-tension of aqueous solutions. *C. Forch. Wied. Ann.* **68**, *801* (*1899*). — After a short discussion of the various methods of measuring surface-tension the author concludes that the drop method is the best for obtaining a large number of comparative results. He accordingly makes a study of the weight of drops issuing from an orifice and finds that it varies with the speed, but that a linear relation is found to hold between the weight of drop and the speed of dropping for limits of 3 to 6 seconds between each drop. He, therefore, adopts a "drop time" of from 4 to 6 seconds in his experiments and reduces all to a standard time of five seconds. A large number of organic and inorganic salts and acids are treated with many interesting results. In conclusion the author quotes the formula of MacGregor and Archibald connecting the degree of dissociation and concentration with the properties of the solution and claims that although a linear relation may be foreseen to hold for certain of the highly dissociated salts, yet it is not so clear that it could be said to hold for less dissociated salts. *H. T. B.*

PHYSICAL REACTIONS AND THE MASS LAW

BY AZARIAH T. LINCOLN

If a number of chemically homogeneous substances react according to what are known as the laws of definite and multiple proportions, they are said to react chemically. This definition is the one employed to distinguish a chemical from a physical reaction. When a state of equilibrium has been established in such a reaction, the relation of the reacting substances can be expressed by what is commonly known as the Law of Mass Action. In the mathematical expression of this law, all the exponential factors are integers, as is implied by the definition of a chemical equilibrium.

In 1894, Professor Bancroft pointed out that the Mass Law could be applied to a class of conditions of equilibrium in which the exponential factors of the mathematical formula representing this equilibrium are not necessarily integers, and are usually not integers. The first case he considered was that of two non-miscible liquids and a consolute liquid. He further applied it to two partially miscible liquids and a consolute liquid, and more recently has shown its application to the cases where one or more of the phases are solids, i. e., to the precipitation of a salt by a liquid or by another salt. This general formula has been looked upon as empirical and, owing to that fact, the subject has perhaps not received as much attention as it would, if it could be established that the formula is *not* empirical, but that it is the mathematical expression of a *new* Law of Nature.

In view of the far-reaching application of this general so-called empirical formula, this investigation was undertaken in order to determine to what degree of accuracy the formula really does represent the experimental facts, and to ascertain over what range of concentration the results agree with those required by the theory. The simplest case has been chosen, i. e., that of two non-miscible liquids and a consolute liquid. Of this class, that system has been selected for which the equilibrium of saturation is represented, apparently, throughout the whole range of concentration, by one curve,—the system of benzol, water and alcohol.

Before taking up the experimental work, I desire to present a cursory résumé of the theoretical considerations which Professor Bancroft has presented cn this subject in his various papers.[1] In my presentation I have followed him very closely and have used his exact words in many cases, in order to describe the phenomena and in the derivation of the formulas. Since I have followed him in this manner, I have omitted all quotation marks.

The application of the Mass Law to the case of two non-miscible liquids and a consolute liquid will be considered first. Let the amount of the consolute liquid S (say alcohol) remain constant, c_1 represent the amount of one non-miscible liquid, A (water), and c_2 the amount of the other, B (benzol) when the solution is saturated at a constant temperature. Then $c_1^{\alpha} c_2^{\beta} = K$, where the exponents α and β are not necessarily integers, but have the usual significance as in other Mass Law equations. If $\frac{\alpha}{\beta} = n$ then $c_1^n c_2 = K_1$, or

$$n \log c_1 + \log c_2 = \log K_1. \qquad (1)$$

This equation is in the form of the equation of a straight line, for if the logarithms of the quantities of the non-miscible liquids be plotted — the log c_1 along the x axis and the log c_2 along the y axis,—the plotted results will be found to be represented by a straight line, the slope of which is n. The equation of a straight line being $Ax + By + C = 0$, or $\frac{A}{B} x + y = -\frac{C}{B}$ (constant), it is readily seen that the above equation (1) is in this form. Instead of designating these quantities by c_1 and c_2, x and

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[1] Am. Acad. Arts and Sciences, 30, 324 (1894); Phys. Rev. 3, 21 (1895); Jour. Phys. Chem. 1, 34, 403, 760 (1897).

y will be used hereafter to represent the amount of the two nonmiscible liquids, A and B, respectively. Then the equation becomes

$$x^{\alpha} y^{\beta} = C_1 \qquad (I_1)$$

While it is a simple matter to plot three variables in a plane, no method is known by means of which this can be done for the logarithms of the variables. So the method employed in this work is to keep one of the variables constant and plot the other two on logarithmic coordinates. Since the formula is hyperbolic, the resulting curve is a straight line. From this the constants can be obtained much more readily than by substituting in the equations, and solving for two unknown quantities.

It is obvious that the form of the equation is independent of the nature of the units employed in expressing the amounts of the substances used. In the equation as deduced above, cubic centimeters have been used as the unit to express the quantity of A and B in a definite volume of the consolute liquid, S. If we desired to express the quantities in grams, there would be a constant ratio,—specific gravity or reciprocal of the specific gravity — between the unit of volume x and that of weight x_1, hence $x = kx_1$. If this value be substituted for x and an analogous one for y, it readily appears, since the constants could be all grouped together, that we would still have an equation of the same form as Equation I_1, and the exponential factors would remain unchanged. The only change will be in the value of the integrating factor log C_1, hence the measurements may be expressed in any convenient unit; but x and y need not necessarily be expressed in the same unit, though it will probably always be more practical to do so. Since the value of C_1 is a function of the nature of the units of which x, y and z (the amount of the consolute liquid, S) are expressed, the weight constants are different from the volume constants. As the constant depends on the absolute value of the exponential factors α and β, it would no doubt be better to calculate the integrating constant by using the rational exponents α and β; but only their ratio can be determined by a study of the equilibrium in one liquid layer.

The formula $x^\alpha y^\beta = C_1$ is not satisfactory, for it does not permit the variation of the consolute liquid provided one of the non-miscible liquids is kept constant, and also because either a change in the unit in which x and y are expressed or a change in the amount of the consolute liquid employed affects the value of the constant. According to Gibbs, the absolute mass of a phase has no effect on the equilibrium, therefore increasing the quantities of x and y m-fold involves increasing the consolute liquid m-fold, if the solutions are to remain at the point of saturation. This would increase the value of C_1 $m^{\alpha+\beta}$ times. If x and y denote values in cubic centimeters of the two non-miscible liquids, A and B, z, the corresponding value of the consolute liquid, S, we have as the equation of equilibrium for saturation

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

If z is kept constant, this simplifies to $x^\alpha y^\beta = C_1$, which is the case we have been considering. If y is constant, we have

$$\frac{x^\alpha}{z^{\alpha+\beta}} = C_2.$$

This is the case in the volumetric experimental part of this investigation. And, finally, if x is kept constant, y and z varying, we have

$$\frac{y^\beta}{z^{\alpha+\beta}} = C_3.$$

So far, the non-miscible liquids, A and B, have been expressed as certain quantities in a definite quantity of the consolute liquid, S. Now, let us see what the effect upon the form of Equation I would be if these quantities are expressed in terms of the total volume of the solution. If there is no contraction or expansion, the volume of the solution will be the sum of the components, i. e., $V = x + y + z$, and the volume concentrations will be

$$\frac{x}{x+y+z}, \quad \frac{y}{x+y+z} \text{ and } \frac{z}{x+y+z}$$

respectively. This simple case occurs very rarely, if ever, and the volume is an unknown function of the component volumes and may be represented by the expression $V = F(x, y, z)$. From the equation $\frac{x^{\alpha} y^{\beta}}{z^{\alpha+\beta}} = C$ we have

$$\alpha \log x + \beta \log y - (\alpha + \beta) \log z = \log C.$$

Now $\alpha \log V + \beta \log V - (\alpha + \beta) \log V = 0$ and subtracting the latter from the former we have

$$\alpha \log \frac{x}{V} + \beta \log \frac{y}{V} - (\alpha + \beta) \log \frac{z}{V} = \log C. \qquad (2)$$

But it is apparent that $\frac{x}{V}$, $\frac{y}{V}$ and $\frac{z}{V}$ are the concentrations of x, y, and z respectively in the total volume. So if we consider x, y and z, to denote the volume concentrations instead of having their previous significance, equation (2) may be written $\frac{x^{\alpha} y^{\beta}}{z^{\alpha+\beta}} = C$. Since α, β and C remain unchanged, Equation I represents the series of saturated solutions obtained at constant temperature with any two non-miscible liquids, and a third liquid miscible in all proportions with each of the other two, provided no chemical reaction takes place and the reacting weights of the liquids remain unchanged. We therefore see that it is immaterial in what units x, y and z are expressed.

The equation $x^n y = C$ is the expression which has been found to represent the saturated solutions of two non-miscible liquids in consolute liquid at a constant temperature. As stated above, if the experimental results are plotted on logarithmic coordinates, the resulting curve is a straight line. In most cases, however, the whole range of concentration cannot be represented by one curve, but two are necessary, so that for one set of concentrations the relation $x^{n_1} y = C_1$ holds, while for the other, the relation $x^{n_2} y = C_2$. Unless there are two sets of saturated solutions corresponding to these two different conditions, this cannot be true. That these two sets of conditions do exist has been shown experimentally for a large number of cases, only one of which, however, will be given here for illustration. If to a saturated solution of chloroform, water and alcohol, one adds a drop of water or of chloroform the solution becomes turbid ; but what separates is the same in both cases. It is analogous to a saturated solution of a salt in a mixture of alcohol and water. In either case, there is a precipitate, but in both cases the precipitate is salt, and the solution is saturated with respect to salt, not with respect to alcohol. It is not easy to see what takes place in a system composed of liquids, because the precipitate being itself a liquid, dissolves part of the solution, and the new phase is not composed of pure substance. This need not trouble us, for, theoretically, at any rate, the precipitate may be treated as pure liquid, and the final equilibrium looked upon as due to a subsequent reaction. One of the two curves represents, then, the set of solutions which is saturated with respect to chloroform and not in respect to water. Whether one adds water or chloroform to these solutions, the precipitate is chloroform. The other curve represents the mixtures which are saturated in respect to water, and not in respect to chloroform. Either water or chloroform, when added to these solutions, produces a precipitate of water. These two sets of solutions are easily distinguishable qualitatively, because in the first case the new phase, containing a large percentage of chloroform, is denser than the mixture from which it separates, while in the second case the new phase, containing chiefly water, is lighter than the original solution. The point where the new phase changes from being denser to being lighter than the first phase is the point of intersection of the two curves. At this point only, is the nature of the precipitate determined by the nature of the infinitely small excess added.

Since saturated solutions are non-miscible, we can treat the case of two partially miscible liquids and a consolute liquid as a special case of the two non-miscible liquids and a consolute liquid, which has just been considered and for which Equation I holds. It has been found experimentally that, in the system ether, water and alcohol, if X represents the amount (synthetically) of the saturated solution of water in ether, Y of the saturated solution of ether in water, and if the quantity of the consolute liquid (alcohol) is constant, the formula $X^{\alpha} Y^{\beta} = C$, or if $\frac{\alpha}{\beta} = n$, then $X^{n} Y = C_1 (I_2)$ holds very well. This formula does not express the total quantities of the two partially miscible liquids because there is no term that gives the solubility of the one in the other, so it will be necessary to introduce into our formula such a term, and this we will now proceed to do.

Let s represent the solubility of one of the partially miscible liquids A (ether), in the other B (water), and s_2 the solubility of the one, B, in the other, A. Then the total quantity of these liquids in one saturated solution will be $X = A + s_1A$, and in the other $Y = B + s_2B$, where A is the quantity of the more abundant liquid, i. e., the solvent, and s_1A is the quantity of the other liquid, the solute, in X, and B the solvent, and s_2B the amount of the solute in Y. But as there is usually some contraction or expansion when liquids are mixed, let the ratio of the actual volume to the sum of the component volumes be σ_1 for the saturated solution of B in A and σ_2 for the saturated solution of A in B. Introducing these factors we have

$$X = \sigma_1(A + s_1A) \text{ and } Y = \sigma_2(B + s_2B).$$

Now substitute these values of X and Y for those quantities in Equation I_2 we have

$$[\sigma_1(A + s_1A)]^n[\sigma_2(B + s_2B)] = C_1,$$

which may be written

$$(A + s_1A)^n (B + s_2B) = \frac{C_1}{\sigma_1{}^n \sigma_1}. \qquad (3)$$

The total quantities of the two pure liquids x and y dissolved in the constant quantity of the consolute liquid are therefore respectively

$$x = A + s_2B \text{ and } y = B + s_1A.$$

Solving these two equations for A and B we find that

$$A = \frac{x - s_2y}{1 - s_1s_2}, \text{ and } B = \frac{y - s_1x}{1 - s_1s_2}.$$

Substituting these values in equation (3) we have

$$\left[\frac{x - s_2 y}{1 - s_1 s_2} + \frac{s_1(x - s_2 y)}{1 - s_1 s_2}\right]^n \left[\frac{y - s_1 x}{1 - s_1 s_2} + \frac{s_2(y - s_1 x)}{1 - s_1 s_2}\right] = \frac{C_1}{\sigma_1{}^n \sigma_2},$$

which simplifies to

$$\left[\frac{1 + s_1}{1 - s_1 s_2}(x - s_2 y)\right]^n \left[\frac{1 + s_2}{1 - s_1 s_2}(y - s_1 x)\right] = \frac{C_1}{\sigma_1{}^n \sigma_2} \text{ or}$$

$$(x - s_2 y)^n (y - s_2 x) = \frac{C_1}{\sigma_1{}^n \sigma_2}\left(\frac{1 - s_1 s_2}{1 - s_1}\right)^n \left(\frac{1 - s_1 s_2}{1 + s_2}\right),$$

and becomes

$$(x - s_2 y)^n (y - s_1 x) = \frac{C_1(1 - s_1 s_2)^{n+1}}{\sigma_1{}^n \sigma_2(1 + s_1)^n (1 + s_2)} \qquad (4)$$

Now since s_1, s_2, $\sigma_1{}^n$ and σ_2 are constant for a constant temperature, we can place the right-hand member equal to a new constant, C_2, whence the relation between C_1 and C_2 becomes

$$\frac{C_1}{C_2} = \frac{\sigma_1{}^n \sigma_2(1 + s_1)^n (1 + s_2)}{(1 - s_1 s_2)^{n+1}}$$

and the equation (4) becomes $(x - s_2 y)^n(y - s_1 x) = C_2$. If, as in the derivation of Equation I, we eliminate the arbitrary quantity of the consolute liquid we have

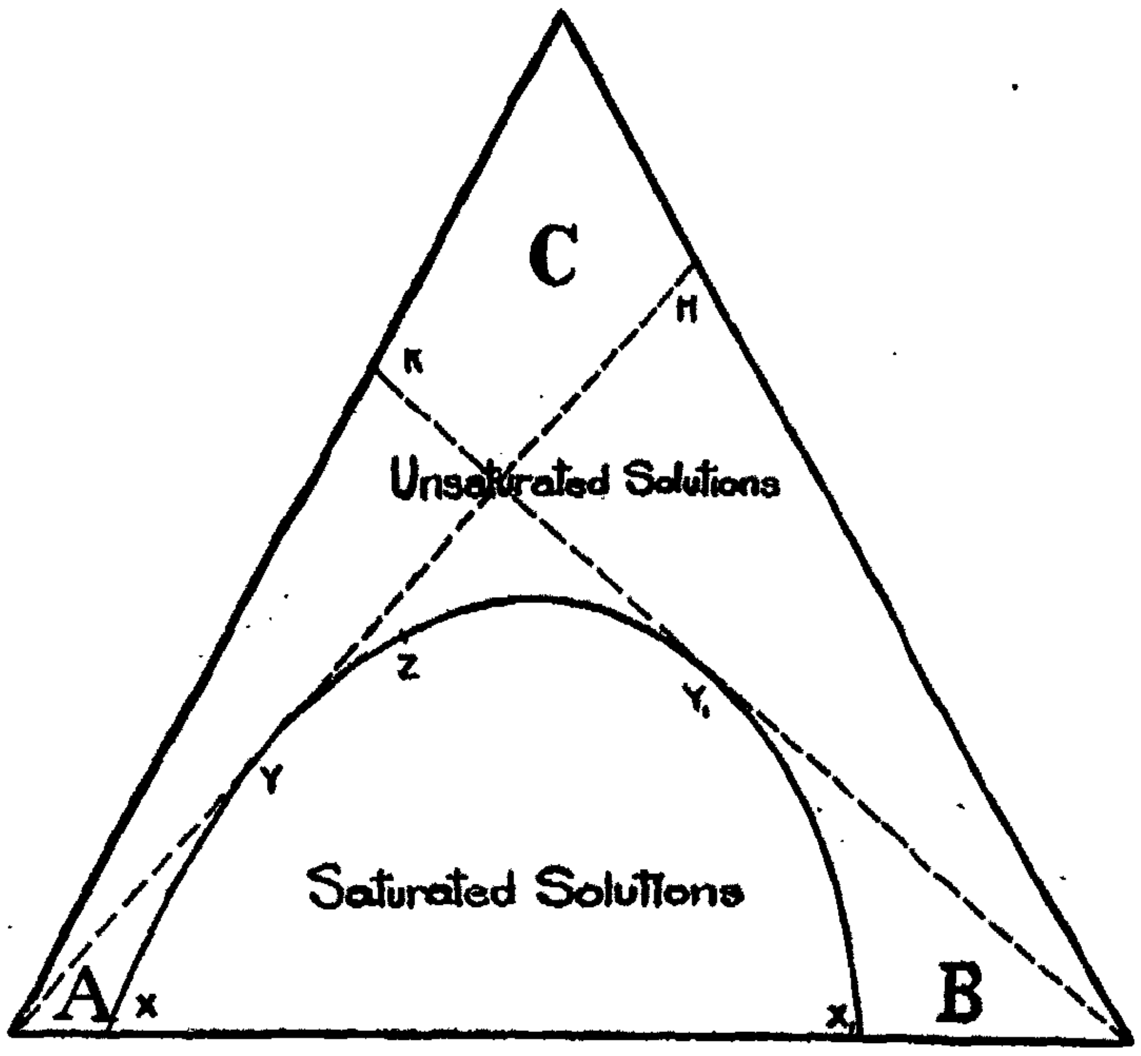
$$\frac{(x - s_2 y)^n (y - s_1 x)}{z^{n+1}} = C_3, \text{ where } C_3 = \frac{C_2}{z^{n+1}}.$$

Now expressing this in the most general form, and thus making it correspond to Equation I, we have

$$\frac{(x - s_2 y)^\alpha \, (y - s_1 x)^\beta}{z^{\alpha+\beta}} = C. \qquad \text{(II)}$$

Equation II is more general than Equation I, the latter being merely a special case of the former, where the terms representing the mutual solubility are so small that they can be neglected.

As has been pointed out above, two curves are necessary to represent the state of equilibrium for saturated solutions over the whole range of concentration for two non-miscible liquids and the consolute liquid. The case of two partially miscible liquids and the consolute liquid is somewhat more complicated, as four curves are required to represent the states of equilibrium corresponding to the four series of saturated solutions. That this is the case can perhaps be best shown by means of a triangular diagram.



Let the corners of the equilateral triangle A, B, and C represent phases containing one hundred percent of the components, and it readily follows that the composition of any phase containing all three components is represented by some point within the triangle. The phases containing only A and B would be represented by the line AB, and if they are non-miscible, the curve representing the concentration of the saturated solution would start from the corners (A and B) of the triangle. Since ether and water are partially miscible, the composition of the solution of ether saturated with water would be represented by some point as x, and the saturated solution of ether in water by x_1. The solutions represented by the line Ax would be saturated with respect to water but not in respect to ether, while the solutions represented by x_1B would be saturated in respect to ether but not to water. The series of saturated solutions of ether, water and alcohol at constant temperature may be represented schematically by the isotherm $x\,y\,z\,y_1\,x_1$. If one starts with the liquid phase designated by x and varies the three components, the line $x\,y\,z$ would represent one series of saturated solutions. From x_1 the same point z would be reached and the curve $x_1 y_1 z$ would represent the composition of the other series of saturated solutions. So by starting with the concentration designated by either x or x_1 and varying the composition, the same concentration of saturation as represented by the point z would be reached, where the two solution phases become identical. Hence the isotherm $x\,y\,z\,y_1\,x_1$ represents the series of saturated solutions of the three components which are in equilibrium at a definite constant temperature. Above and outside of this isotherm is the field of unsaturated solutions and the portion of the figure included by the curve represents the field of mixtures which separate into two liquid phases, the composition of which is given by some two points on the isotherm. Since the isotherm represents the composition of those saturated solutions in equilibrium, the addition of the component A or B will cause clouding, and now let us inquire whether it makes any difference which of the constituents is added. We saw that the location of x was due to the saturation of A by B, so any further addition of A would not cause clouding of this solution, but as we follow up the isotherm there must come a point where the addition of A will cause clouding. Such a point y is where the line AH drawn through A is tangent to the curve. The same is true for the addition of the component B, the line BK through B being tangent to the curve at y_1. It has been shown experimentally[1] that if to a mixture of C and B containing less of B than indicated by

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[1] Schreinemakers. Zeit. phys. Chem. 23, 652 (1897); Pfeiffer. Ibid. 9, 469 (1892).

H, A be gradually added, clouding will eventually take place and the mixture separate into two liquid phases; but if A be added to a mixture of B and C containing more of B than indicated by H, no clouding will result. The same reasoning may be applied to the addition of B to solutions of A and C containing less or more of A than indicated by K, clouding occurring in the first case and not in the second. It is therefore apparent that the isotherm is divided into four parts which correspond to the following four distinct sets of equilibrium:

1. The solutions represented by the line xy are saturated with respect to B, and an excess of A does not produce a precipitate.
2. The solutions represented by the line yz are saturated with respect to B, and an excess of A or B produces a precipitate of B.
3. The solutions represented by the line $z\,y_1$ are saturated with respect to A, and an excess of A or B produces a precipitate of A.
4. The solutions represented by the line $y_1\,x_1$ are saturated with respect to A, and an excess of B does not produce a precipitate.

Equation II has been tested for a large number of partially miscible liquids which included a great many esters. The agreement between the experimental results and those required by the theory is perfectly marvelous, and therefore shows that the facts are very well represented by the formula.

A number of salts form two liquid layers with ethyl alcohol as well as with a number of other solvents. In some cases, one of these layers disappears upon standing, in other cases they are permanent, while in still other cases we have a liquid layer and a solid. Having all these various stages of the phenomenon thus presented, it is held by some that a salt, in precipitating out, first separates as a second liquid layer and then passes into the solid phase, more or less rapidly, depending upon conditions. From this point of view, it is a natural step to replace one of the two non-miscible liquids as considered in the preceding by a solid phase and inquire if the equilibrium of this system can be represented by the general formula as given in Equation I.

In the case where the liquids were partially miscible, terms were introduced into the equation in order to take this factor into consideration; and in this case, it will be necessary to modify the equation so that it will express the fact that when the quantity of the consolute liquid is zero the concentration of the salt in the water is not infinite. In order for the formula to express this, it may be modified in several ways; but as the method of moving the coordinates has been the one employed, this method only will be considered here.

If to x we add some constant, A, Equation I, then takes the form

$$(x + A)^{\alpha} y^{\beta} = C_1, \text{ or if } n = \frac{\alpha}{\beta} \text{ we have}$$

$$(x + A)^{n}\, y = C_1. \qquad \text{(III)}$$

The same principle applies if the two non-miscible liquids are replaced by two salts. The equation would then take the form

$$(x + A)^{n}\, (y + B) = C_2. \qquad \text{(IV)}$$

This is the case of the precipitation of one salt by another.

Here, as in the case of two non-miscible liquids, we have two curves, along one of which the solid separates out and along the other the liquid, when only one of the original phases is a solid; but when two solids replace the two non-miscible liquids, we have two curves as in the other cases, along one of which the solution is saturated with respect to one salt and along the other with respect to the second. The intersection of the two curves comes at the concentration at which the two salts separate, side by side; i. e., the two salts are in equilibrium with both the solution and the vapor.

That this is what does take place is apparent from the experimental data collected by Bodländer, Gérardin, Antusch and Holleman, Nicol, Engel, Stetchenow, Linebarger, and others. When these experimental results are interpreted in the light of the Mass Law, it is found that Equations III and IV represent the facts to a fair degree of accuracy. Taylor[1] and Bathrick[2] were able to eliminate some of the experimental errors and found by so doing that they approximated more nearly the values required by these formulas.

In the previous work on the system of benzol, water and alcohol, no extra precautions were taken to obtain chemically pure substances; but the alcohol and benzol were treated with dehydrating agents in order to render them free from water. The mixtures were prepared synthetically by volumetric means and the best results thus obtained show an experimental error of about two percent. It was desired to learn if a nearer approximation to the absolute amounts of the three constituents in equilibrium could be made by employing gravimetrically prepared mixtures of the carefully purified substances. Having thus determined (synthetically) the amounts of the constituents, it will be shown how well this equilibrium can be represented by the Mass Law. The experimental work will now be presented.

The water used was obtained by treating the distilled water of the laboratory with barium hydroxide, in contact with which it remained for several days. The water was then decanted off and distilled. A block-tin condenser was used and only the middle third of the distillate was collected and employed in this work. One portion of the alcohol used was prepared by treating absolute alcohol with lime for about a day, decanting off and fractionating. This fractionated portion was treated with anhydrous copper sulphate in contact with which it remained for about two days. The alcohol was then decanted off and fractionated by the aid of a Hempel column. This distillate was redistilled by means of the same apparatus, and the portion coming over at 77.4° was collected. The temperature did not vary more than 0.1°, while the barometer only varied from 746 to 748 mm. The distillate was protected from the air, during the process of distilling, by means of a tube filled with calcium chloride. The

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[1] Jour. Phys. Chem. 1, 718 (1897).

[2] Ibid. 1, 157 (1896).

other portion of alcohol employed was prepared by heating ordinary alcohol (95 percent) with quicklime for about a day. This was then decanted off and treated twice again in the same manner, — a reverse condenser being employed and the alcohol was boiled with the lime for about seven hours each time. During the last boiling, the lime remained in large hard lumps and from these the alcohol was decanted off and fractionated by the aid of a long Hempel column. This distillate was again distilled. This time we employed a Hempel column about 40 cm long, in which was a coil of lightly wound copper gauze about 16 cm long and a large quantity of glass beads, all of which was kept at a constant temperature by a hot water jacket. The temperature of that portion collected ranged from 76.8° to 77.1° (the thermometer was completely immersed in the vapor) while the barometer varied from 728 to 733 mm. From the experimental results, it was found that these two samples of alcohol were of the same degree of purity. (Compare 1, 2, and 3 with 4 and 5, under No. 7, Table II. The determinations within the brackets are with the second portion of alcohol.)

The benzol was purified by shaking it with successive portions of concentrated C. P. sulphuric acid, until upon further addition of sulphuric acid and permitting it to stand for twenty-four hours, no color whatever was imparted to the acid. Having thus extracted the thiophene, the benzol was then washed several times with water, twice with dilute caustic potash, and then with concentrated caustic potash in order to remove the last trace of sulphonic acid. The benzol was then washed several times with water, and dried over fused calcium chloride in contact with which it remained for two days. The benzol was then decanted off and distilled. A Hempel column was employed and the boiling point of the portion collected varied from 78.8° to 79.2°, while the barometer readings ranged from 740 to 746 mm. This distillate was further purified by crystallizing twice. A sample was then tested for thiophene by means of isatin and not the slightest trace was detected.

These liquids were all preserved in bottles which had been thoroughly cleaned and then steamed for at least a day each. The burettes and pipettes were carefully calibrated. The burettes, by means of which the alcohol and water were delivered, were fastened to the bottles and the connection made in such a manner as to enable one to draw the liquids out by suction. In the case of the alcohol, the cork was cemented in with paraffin and the alcohol further protected from the moisture of the air by means of two large tubes filled with fused calcium chloride. The little flasks in which the mixtures were prepared were thoroughly cleaned and then steamed.

All the experiments were made at 25° C. unless otherwise designated. The temperature of the bath was maintained constant by means of a thermostat similar to that of Ostwald's, except that the bath was stirred by means of a small hot-air engine. There was no particular difficulty experienced in keeping the temperature within 0.2° for a day.

The experiments were performed by running into a 100 cc flask, — or into a 250 cc flask — 5 cc of benzol by means of a pipette, then into this a definite quantity of water from the burette. The alcohol was then added gradually until about enough was present to make the solution homogenous. The flask was usually kept in a beaker of water two or three degrees above 25°. After enough alcohol had been added to make the solution clear, the flask was tightly stoppered and placed in the bath where it remained long enough to assume the temperature of the same. If the solution became cloudy or opalescent, more alcohol was added, the solution warmed up, and then the flask was put back into the thermostat. This process was continued until it was found that enough alcohol had been added to make the contents of the flask one homogeneous liquid at 25° and the average of the two last readings of the quantity of the alcohol was taken as the quantity necessary to make the solution clear. One drop of either water or benzol would cause the solution to separate into two liquid layers.

At first I tried to determine the different points by adding to 5 cc of benzol a definite quantity of water and then enough alcohol, in the manner described above, to make a homogeneous liquid; then adding to this another definite quantity of water, and clearing with alcohol and so forth, until a number of points of saturation had been determined by employing different quantities of water and alcohol, but the same portion of benzol. It was soon discovered, however, that these respective points of equilibrium could not be exactly duplicated, owing to various experimental difficulties which will be mentioned subsequently. The results given in Table I are the average of three or more separate determinations for each point, wherein a separate portion of benzol was taken each time.

The volumetric results are given in Table I. In the first column, x, is given the number of cubic centimeters of water, in the second column, z, the number of cubic centimeters of alcohol found by experiment, while in the third column, the number of cubic centimeters calculated, and in the last column, log C, the logarithm of the constant.[1]

TABLE I

5 cc. benzol. $\frac{x}{z^n} = C : n = 1.525 : \log C = 0.9812.$

x water	z alcohol found	 calc	log C
1.31	5.25	5.252	0.9837
3.40	9.81	9.816	0.9808
4.51	11.82	11.81	0.9816
5.09	12.80	12.79	0.9818
8.15	17.39	17.41	0.9803
9.63	19.38	19.43	0.9796
13.50	24.23	24.25	0.9808
19.13	30.46	30.47	0.9810
24.65	36.42	35.98	0.9892
27.75	39.32	38.89	0.9885
35.07	45.88	45.27	0.9890
49.55	57.43	56.79	0.9876
69.37	72.68	72.00	0.9975

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[1] The formula employed by S. F. Taylor was $x^n y = C$, where $n = 1.85$. If this be expressed in the form of the equation used we should have $x/z^n = C$, where $n = 1.54$ as against 1.525 employed by me. Or if the formula I used be changed to the form $x^n y = C_1$, $n = 1.90$ as against 1.85 employed by Taylor.

It will be observed that the found values agree very well with the calculated values, particularly in the first half of the series; but the agreement in the remainder of the series is not as good, the difference exceeding one percent in some cases.

Several sources of error were observed in the volumetric method, and as these could be partially eliminated by weighing out the quantities of liquids used, a series of observations was made gravimetrically. The same general method of procedure was employed as that described above, only the quantities of the liquids used were determined by direct weighings instead of measuring them out.

In Table II are given the results obtained gravimetrically. In the first column, y, are the number of grams of benzol, in the second, x, the number of grams of water, and in the third, z, the number of grams of alcohol used. In the fourth column "calc," are the number of grams of alcohol required by the formula for equilibrium, while the logarithm of the constant appears in the last column. In this table the separate determinations for the different points are given, and not the average, as in the preceding table.

It will be noticed that the found and calculated values agree very closely; in most cases the variation is less than *1/3 of one percent.* In the case of points 9 and 12, the agreement is not quite so good, but it is only a question of determining these points more carefully in order to make them fall into line. This I did not attempt to do.

It was thought worth while to repeat Taylor's[1] work and see if the exponential factor really remains constant over a considerable range of temperature. A few determinations were made at 10° C and the results are tabulated in Table III.

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[1] Jour. Phys. Chem. 1, 301 (1897).

TABLE II

Formula $\frac{x y^{n-1}}{z^n} = C : n = 1.525 : \log C = 0.49494$

	y benzol	x water	z alcohol		log C
			found	calc	
1	79.318	2.058	15.362	15.28	0.4987
	82.269	2.078	15.761	....	0.5032
2	72.593	5.016	26.496	26.57	0.4932
	72.549	4.944	26.324	26.31	0.4951
3	4.3798	1.3053	4.1882	4.181	0.4962
	4.3753	1.3169	4.198	4.197	0.4940
4	4.372	3.388	7.816	7.825	0.4955
	4.373	3.398	7.835	7.810	0.4957
5	4.361	4.469	9.376	9.356	0.4964
	4.361	4.499	9.386	9.397	0.4941
6	4.374	5.093	10.196	10.21	0.4889
	4.376	5.116	10.248	10.23	0.4957
7	4.373	9.678	15.402	15.54	0.4889
	4.375	9.687	15.533	15.56	0.4939
	4.393	9.687	15.457	15.58	0.4898
	[4.383	9.632	15.369	15.51	0.4884
	4.378	9.618	15.379	15.49	0.4903]
8	4.376	13.509	19.346	19.35	0.49496
	4.369	13.507	19.284	19.33	0.49317
9	4.387	19.236	24.211	24.42	0.4854
	4.386	19.227	24.155	24.41	0.4876
10	4.379	27.899	31.150	31.14	0.4951
	4.380	27.947	31.234	31.18	0.4962
11	4.377	35.244	36.497	36.36	0.4974
	4.376	35.227	36.548	36.34	0.4988
12	4.402	49.725	46.120	45.61	0.5024
	4.408	49.788	46.177	45.63	0.5029
13	4.387	69.776	56.916	56.84	0.4959
	4.381	69.638	56.912	56.73	0.4970

TABLE III

Formula $\frac{xy^{n-1}}{z^n} = C : n = 1.525 : \log C = 0.57666$

	y benzol	x water	z alcohol		log C
			found	calc	
1	4.390	3.353	8.768	8.788	0.5752
	4.390	3.436	8.943	8.93	0.5777
2	4.405	5.050	11.535	11.51	0.5773
	4.404	5.044	11.495	11.50	0.5765
3	4.368	24.772	32.441	32.56	0.5743
	4.372	24.827	32.674	32.63	0.5752

Average = 0.576665

These results corroborate Taylor's work and show that over a considerable range of temperature the same exponential factor applies. It will be noted that the calculated values here agree as closely with the found values as did most of the results in Table II, i. e., within *1/3 of one percent.*

As there were a number of experimental difficulties encountered, I will mention a few of them. The first difficulty met with was determining the exact point when the solution became clear. As described above, the alcohol was added until the solution became perfectly clear and the average of the last two readings was taken as the quantity of alcohol necessary to make the mixture a homogeneous liquid. It was, therefore, necessary to take these last two readings as close together as possible. Over a certain range of the concentrations, that is, when the solution separates into two liquid layers that are approximately equal in size, the transition from the cloudy to the clear liquid is very gradual. There is no decidedly marked change. The cloudy liquid becomes less and less cloudy, and this changes into a decidedly opalescent tint, the intensity of which decreases very slowly until the last trace of opalescence has disappeared and the solution is clear. This state of affairs holds over quite a range and includes the first five or six points given in Table II.

For the remainder of the series, another standard had to be employed, that is, the appearance of the second liquid layers in the form of fine globules. Many times it was very difficult to distinguish these from fine foreign particles that appear as lint, which will get into the solution whatever precautions one may take. Hence having these two different points on which to set, as it were, for different parts of the series of concentrations, is one source of error.

As previously described, the small flasks and their contents were heated several degrees above 25° and then placed in the bath (at 25°) and allowed to cool down to that temperature. Unless these are frequently shaken, the contents will separate into two liquid layers; but this can be prevented, provided the point of equilibrium has been reached, by agitating the flasks considerably. On removing the flasks from the bath, in order to shake them, the surface is cooled, the vapor is condensed, and cloudiness results. Then, too, the same difficulty is experienced when the flask is removed from the bath, in order to ascertain whether the solution is clear. This latter difficulty was gotten around by keeping the flask in a beaker of water in the bath and by removing the beaker and its contents from the bath together. The observations had to be made through the beaker and a considerable layer of water; but by renewing the water in the bath frequently, it could be kept clear. Even this did not always prevent the sides of the glass from becoming coated, which gave the appearance of a slightly opalescent tint.

While making the volumetric determinations, particularly, a considerable time would elapse between the addition of the successive portions of the alcohol, while the flask and its contents were assuming the temperature of the bath. During this time, the alcohol would evaporate from the point of the burette, and if there were many of these intervals, the quantity of alcohol evaporated would amount to considerable — several hundredths of a cubic centimeter.

In order to insure homogeneity in the liquid, it was necessary to heat the solution several degrees above the temperature at which we desired to determine the equilibrium. If alcohol is added while the liquid is at this higher temperature, there will be loss due to the escape of the vapor phase, and consequently the higher this temperature the greater the loss. The greater the number of additions of alcohol, the more times the flask has to be opened; if this is done at the higher temperature, the loss is yet still greater. This was more of a source of error during the volumetric determinations, whereas during the gravimetric determinations I aimed to eliminate this error by cooling the flask below 25° before opening it in order to introduce the alcohol.

During the volumetric measurements, it was observed that the determinations of the same point on different days and even at different times of the same day, were annoyingly just far enough apart so as to make it a little difficult to tell what the real values for that particular point were. This was found to be due partially to the temperature coefficient of the benzol. The benzol was supposed to be kept constant in these experiments, and was measured out by means of a 5 cc. pipette. The temperature of the room was as low as 14° some mornings when the benzol was measured, while at other times it was as high as 21°. That this was the cause of the errors became very manifest when the determinations were made gravimetrically. This can be seen very readily by looking at the first column in Table II. The amounts of benzol delivered by this pipette ranged from 4.361 grams to 4.408, which is a difference of about one percent. This is not all experimental error, for by observing the quantities of benzol delivered for any particular series of experiments, i. e., at the same time, it will be seen that the variation is only a few units in the third decimal place. (See the values given under 4, 6, 10, 12, etc., Table II.) This source of error has been eliminated by taking the quantities of the components by weight, and hence regarding them all as variables.

While making the determinations at 10° it became apparent that a slight variation in the temperature of the bath had a very marked effect upon the equilibrium. Even one-fifth of a degree made a very perceptible difference in the quantities of the components necessary to produce the equilibrium. So at 10° the constancy of the temperature of the bath was a very important factor, and therefore a marked source of error that was to be guarded against. Nor is it reasonable to suppose that this facter wholly disappears at 25°, although in our determination it was not as cautiously guarded against as it was at the lower temperature.

One of the greatest experimental difficulties with which we had to contend was undoubtedly the effect due to the varying intensity of the light. Since a considerable portion of the time, during the period over which the experimentation extended, was cloudy, it was difficult to tell when the solutions which passed through the opalescent stage became clear. This difficulty was overcome to a considerable extent by performing the experiments on bright sunny days, during the middle of the day, and in a few cases by the aid of the electric light. Even a change of the position of the flask would make considerable difference in the appearance of the contents, for if it were held in one position, it would appear perfectly colorless, whereas in another position it would appear decidedly opalescent. Again, if it were held so a ray of sunlight shone upon it, it would appear opalescent, while out of the sun it was apparently clear. One cloudy afternoon I made a determination and concluded that the sufficient quantity of alcohol had been added when 18.980 grams had been run in, and was going to call this completed. Before putting it aside, I turned on the electric light — this was at 3 P.M. — and on doing so the solution appeared decidedly turbid. In order to make the solution perfectly clear, it was necessary to add alcohol until there were 19.346 grams present, thus making a difference of about two percent, owing to the varying degree of intensity of the light in the two cases. I therefore aimed to eliminate this source of error by performing the experiments, as nearly as it was possible, under the same conditions in regard to the intensity of the light.

If a mixture of benzol, water and alcohol, which contains more benzol or water than is necessary for saturation, be allowed to separate into two liquid layers, the composition of these layers will be represented by two points on the isotherm which represent the series of saturated solutions at this particular temperature. The two solutions represented by these two points are known as conjugate solutions, and the line joining them, when the triangular diagram is employed, is known as the "tie-line". If any mixtures are taken, the composition of which is represented by any points on the tie-line, and allowed to separate into two liquid layers, their respective layers will all have the same composition and can be represented by the points where the tie-line cuts the isotherm. Various efforts have been made to determine the composition of these conjugate liquids, and to ascertain the distribution of the benzol and water in the alcohol. It is not a very easy matter to analyze for any of the three components, but if one of them could be determined accurately, the amounts of the other two could be easily obtained by interpolation from the equilibrium curve as determined from the results given in this paper. But, as yet, no satisfactory method has been devised for determining even one of the constituents. Taylor succeeded in making an approximate analysis by determining the refraction of the solutions. Various other methods suggest themselves — such as the determination of the density of the solutions, etc.; but each entails a very great amount of labor. A method, which was tried, was to add a definite quantity of an electrolyte to the solutions and determine the electrical conductivity. This was carried out by adding to 3 cc. of the solution, 5 cc N/50 KCl and 10 cc of alcohol, which was enough to make the solutions perfectly homogeneous, except those at the extreme benzene end. Solutions, the compositions of which were known synthetically, were first employed and the conductivity was plotted against the percentage composition of the alcohol. Having thus determined the conductivity curve, the percent of the alcohol in the other solutions of unknown strength could be readily read off on the curve from their conductivity. Then by finding the point on the isotherm (plotted on the triangular diagram) corresponding to this percent of alcohol, the amounts of the other two constituents could be ascertained. Only approximate results could, however, be obtained. In some cases, if the percentage of the alcohol was not determined closer than 0.5 percent, the interpolated values for benzol and water would vary several percent. When there was only a few percent of benzol, this would make a difference of one or two hundred percent in the quantity of benzol. If the conductivity were plotted against the percent of benzol, the differences were much more marked.

Better results might be obtained by employing an electrolyte, such as acetic acid, which could be added to the solution of benzol, water and alcohol, without forming two liquid layers. This was not tried, however, for it seems apparent that it would be necessary to use large quantities of the solutions in order to meet with any fair degree of success. As the supply of our purified liquids had been exhausted, it was thought hardly desirable to continue this any further at the present time.

From the work with the conductivity method, it was apparent that the results given by Taylor[1] represent the facts in a general way, and they are not far from the correct values. But it is very evident that before the distribution ratio can be determined accurately, it is necessary that a method be devised by means of which the percent of the constituents can be determined within a few tenths of one percent at the outside, and the more accurately the composition can be ascertained, the better.

There are other systems, however, which can be analyzed more easily than this one with which we have been dealing, and with such a system it would be a much easier task to determine the distribution of the two substances in the consolute liquid and show whether the theory holds. It has been shown that in order to prove that the Mass Law is applicable to this class of physical phenomena, very accurate determinations of the amounts of the constituents in equilibrium must be made. So in the determination of the distribution ratio, in order to show that we

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[1] Jour. Phys. Chem. 1, 461 (1897).

are dealing with an *exact* theory, the analysis of the solutions must be made with a very considerable degree of accuracy.

In the presentation of the theoretical consideration, it has been shown that the Law of Mass Action is applicable to a class of reaction which has been, heretofore, looked upon as mere physical phenomena. The Mass Law has been applied to the following classes of reactions:

1. Two non-miscible liquids and a consolute liquid,
2. Two partially miscible liquids and a consolute liquid,
3. Where one of the non-miscible liquids of (1) has been replaced by a solid phase, i. e., to the precipitation of a salt by a liquid,
4. Where both of the non-miscible liquids in (1) have been replaced by a solid phase, i. e., to the precipitation of one salt by another, and
5. To the precipitation of a liquid by a salt.

These various cases have been considered and the formulas deduced (except in 5). Experimental data have not been presented to show how closely the formulas represent the facts; but attention has been called to the work of the various investigators whose results have been interpreted in the light of the Mass Law. Their results show a surprising agreement, considering the fact that the relative accuracy of their experimental work differs considerably. Since the solubility of many of the various solutes have not been determined with any extraordinary degree of accuracy, and particularly in the case of many salts, in the presence of another salt, it is not surprising that the agreement in some cases between the theoretical and experimental results is not any better than it is. It has been shown by the work of some, that when these solubility determinations are made with a much greater degree of accuracy, the experimental and theoretical results agree better, and the more accurately these solubility determinations are made, the more closely do the experimental results approximate to those required by the formula which represents the state of equilibrium for these particular saturated solutions.

In the case of the experimental results presented in this paper, attention has been called to the various sources of experimental error. It has been seen, in the simplest case of ternary mixtures, that a large number of factors enter into the accurate determinations of the point of saturation of solutions of benzol, water and alcohol. Among these experimental difficulties have been mentioned the temperature coefficient of benzol, and no doubt of alcohol, since they both have about the same value; the difficulty of determining the exact point of clouding, owing to the gradual transition from the cloudy mixture through various stages of opalescence to the perfectly clear solutions; the ease of clouding due to the chilling of the walls of the flask on removing it from the bath; the effect on the equilibrium of a slight change in the temperature of the bath, particularly at 10°; the difference due to the change in the intensity of the light. It has been pointed out how the source of error in some cases can be partially removed, while in other cases it can be wholly eliminated. Having overcome many of these difficulties, we find that the experimental results are within about *one-third of one percent* of those required by the theory, and that this agreement extends over a range of concentration from about one part of benzol in 0.025 part of water to one part in 15.92 parts of water, or over a range of from one to 680.

In the face of these data and in view of the facts brought out during the experimental work, it is apparent that the more of the experimental difficulties that can be eliminated, the more closely do the experimental results approximate to the values required by the theory. We are, therefore, justified in concluding that in this particular case — that of the two non-miscible liquids and the consolute liquid — the *formula represents the facts absolutely.*

That this is true for the temperature between 10° and 35° has been shown by others and confirmed by myself; and, as in the case of the application of the Mass Law to chemical reactions, the exponent n is independent of the temperature.

It still remains, however, for subsequent workers to show

how closely the theoretical values can be approximated in other cases. There is apparently no doubt, from the data available at present, that the difficulties in the way of proving that the theory holds absolutely are almost solely experimental. When these shall have been sufficiently eliminated, so as to permit the collection of very accurately determined data, it will be a much easier matter to prove conclusively whether this general formula is empirical or not. But in view of its far-reaching application, and in the face of the present data, it appears that the experimental results are too close approximations to those required by the theory for the formula to be simply an empirical one. There are very strong indications that we have to do here, not with an empirical formula, but with the mathematical expression of a newly discovered Law of Nature; but which still requires the light of more data before it can be unquestionably demonstrated.

This investigation was undertaken at the suggestion of Professor Bancroft, and I take this means of thanking him for his timely suggestions and assistance.

Cornell University,
February 5, 1900

ON THE SYSTEM WATER, PHENOL, AND HYDROCHLORIC ACID

BY W. H. KRUG AND FRANK K. CAMERON

Phenol and water form a partially consolute mixture. If the temperature be sufficiently lowered, solid phenol separates and we have a two-component system with two liquid phases, a solid phase and a vapor phase, and complete equilibrium at a definite temperature. The addition of hydrochloric acid, which is very soluble in water, but slightly soluble in phenol changes the relative miscibility of the two original components and the temperatures at which solid phenol can exist in the altered system is raised. We will now have a ternary system with a solid phase, two liquid phases, and a vapor phase, consequently one degree of freedom, and since neither the water nor hydrochloric acid can separate in the solid phase, the system may not become non-variant so long as the phase liquid phenol persists.

But the case under consideration can be made to assume special features. If we keep the mass of phenol *relatively* small, water is so little soluble in it, that as the solid phenol separates, the concentration of the water hydrochloric acid is but slightly changed, and the freezing temperature of the phenol remains very constant in a similar manner to the case which Nernst has already described.[1]

Qualitatively, the case under consideration has been specifically discussed by Bancroft[2] in a study of ternary systems with two liquid phases, and he found that solid phenol was in equilibrium with liquid phenol and water at + 0.8°, whereas the temperature rose to about 25° when the laboratory acid, presumably

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[1] Zeit. phys. Chem. 6, 30 (1890).

[2] Jour. Phys. Chem. 1, 420 (1897).

a concentrated solution, was used in place of the water. These figures must have been determined as rough approximations, however.

In the experiments here described, we measured the temperatures at which solid phenol separated from its melt in contact with aqueous solutions of hydrochloric acid. The conditions under which the measurements were made, were not the ideal ones suggested by *a priori* considerations. It was soon found to be impracticable to have the volume of water large in comparison with the volume of phenol present. The apparatus used was essentially that of the "Beckmann Freezing-point Method" with slight modifications, but we made it smaller and more compact than usual, materially increasing the convenience and time elements in its use. In stirring the mixture when large amounts of water were used, it was not possible to prevent the phenol from freezing in detached masses throughout the water solution, when its entire mass very rapidly became solid, an undesirable result in itself, and the thermometer registered absolutely noncomparable and confusing readings conditioned by the supercooled water solution. The thermometer was of the Raoult type for freezing-point determinations, gave direct readings on the centigrade scale, and was graduated to tenths, hundredths being readily estimated. The recorded readings on the means of from four to five determinations in each case, the direct variations not exceeding 0.03° in any case. The hydrochloric acid solutions were all made from c. p. acid and distilled water and compared by titration against a very carefully prepared $\left(\frac{N}{5}\right)$ sodium hydroxid solution. The titrations were all made *after* the freezing-point determinations, and any possibility of obtaining prejudiced readings was avoided. The phenol was purified by repeated distillation, first and last portions of the distillate being discarded. It distilled at a constant temperature. It was kept in a flask with a tight-fitting stopper carrying a calcium chlorid drying tube, and when needed, was melted by careful warming, the desired portion being rapidly transferred to the freezing-point apparatus. The hydrochloric acid was at once added, but cautiously, to such amount as somewhat more than saturated the phenol. The thermometer was so adjusted that the bulb was entirely covered by the liquid phenol. The determination was made in the usual manner. The first reading obtained was always discarded, being used simply as an indication as to how far the solution should be undercooled, about 0.3° being the amount of undercooling we considered allowable. The results obtained are given in the following table:

Gms. per liter	Reacting wts per liter	Freezing-point	Gms per liter for 1° rise	Rise of freezing-point per reacting wt
0.0000	0.0000	1.365°	0.000	∞
0.8035	0.0222	1.737	2.159	16.75
1.6154	0.0446	1.883	3.118	11.61
3.4028	0.0941	2.298	3.647	9.91
4.1574	0.1149	2.443	3.856	9.38
8.3009	0.2294	3.048	4.932	7.33
13.1323	0.3629	4.000	4.983	7.26
16.2384	0.4488	4.738	4.814	7.52
21.9251	0.6060	5.603	5.173	6.99
32.8514	0.8965	7.100	5.728	7.51
66.2671	1.8316	12.013	6.223	5.81
130.9690	3.6199	17.078	8.335	4.34
131.3234	3.6297	17.195	8.296	4.36

With hydrochloric acid in excess, the freezing-point of the phenol[1] was 25.26°.

The first column gives grams of hydrochloric acid per liter of solution. The second reacting weights of hydrochloric acid per liter. The third, the observed temperature readings. The fourth, the number of grams hydrochloric acid per liter corresponding to a rise of 1° in each case. The fifth, the rise of temperature corresponding to one reacting weight per liter of solution, in each case.

These results are indicated on the accompanying chart. It has seemed desirable to select grams hydrochloric acid per liter as abscissæ, and for convenience in illustrating, they are divided

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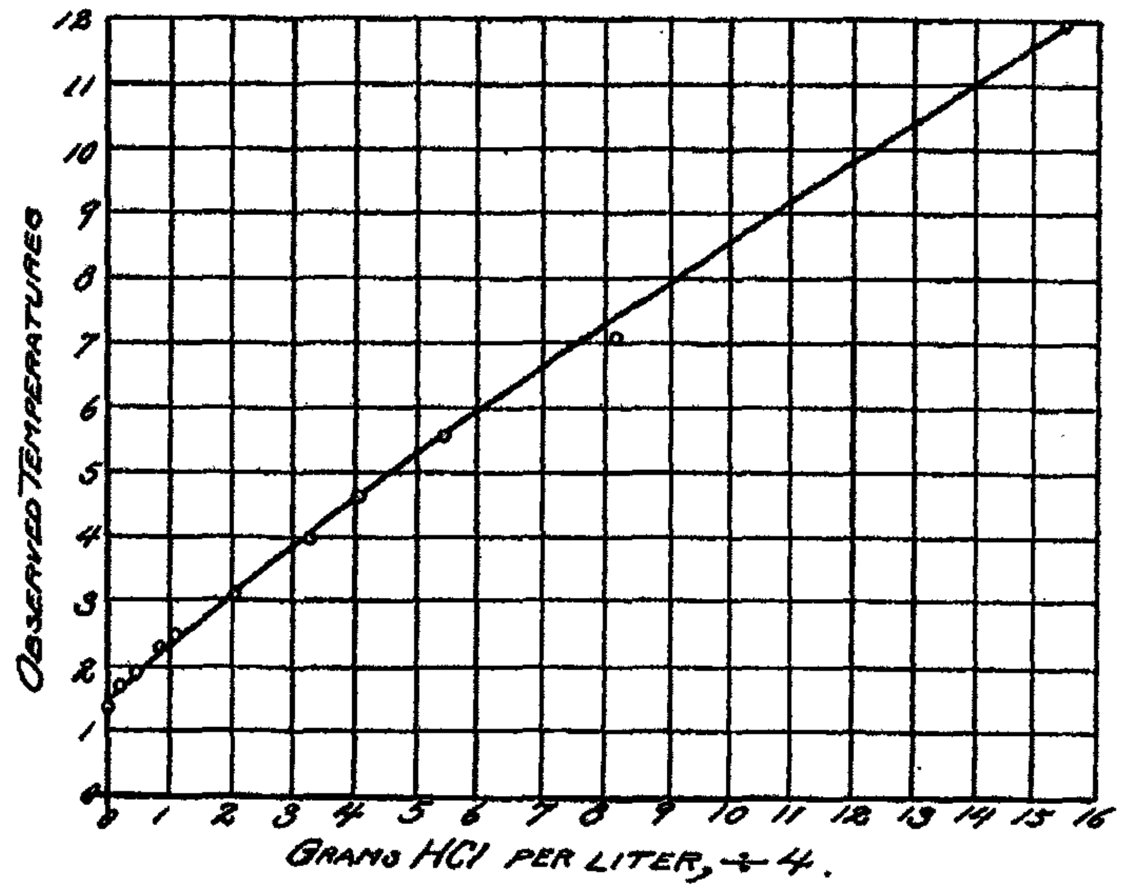
[1] The phenol used melted at 40° C and distilled constantly at 176.5° C.

throughout by four. The ordinates represent the corresponding temperatures found. The curves, even as charted, and especially that part illustrating the lower concentrations, is quite flat, approximating a straight line. But the fourth column of the table shows undoubtedly a curvature exists. The fifth column shows that the curve would be of practically the same nature if



plotted with reacting weights as coordinates. The upper part of the curve appears to approach parallelism to the axis of abscissæ.

It has been suggested by Bancroft that this method be used for standardizing hydrochloric acid solutions, thus doing away with the tedious weighings, filterings, etc. involved in the usual procedure. By reference to the fourth column it will be seen that the accuracy of the method is dependent on the concentration. For solutions about $\left(\frac{N}{10}\right)$ *tenth-normal*, it will be seen that an error of 0.01° corresponds to less than 0.04 gram per liter. But we are convinced from our experience, that even in the hands of an expert, it is not safe to assume a less error than 0.02°

in determining unknown solutions, unless indeed unusual care be observed and a thermometer reading to thousandths of a degree be used. Therefore, while the method should prove a useful and rapid one for making up solutions of approximately known strength, it is not sufficiently refined for the requirements of good analytic practice. And in consequence, it did not seem worth while to standardize our thermometer, or to attempt a further and more accurate determination of the curve.

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ON TWO THEOREMS OF GIBBS

BY PAUL SAUREL

Among the many results contained in Gibbs's famous memoir are two important equations.[1] The first of these is a relation between the changes of pressure and temperature in a univariant system; the second is a relation between the changes of pressure, temperature, and chemical potential in a divariant system, and this equation, when certain conditions are satisfied, takes a form analogous to that of the first. Gibbs shows, in the special case of one component, that his equation for univariant systems is equivalent to the Clapeyron-Clausius formula.

The object of the present note is to show that, in the general case of n components, Gibbs's equation for univariant systems is equivalent to the Clapeyron-Clausius formula, and that the equation for bivariant systems can, when the conditions referred to above are satisfied, be likewise put into the form of the Clapeyron-Clausius equation.

For this purpose we shall start with the following equation, which is established by Gibbs:

$$v' dp = \eta' dt + m'_1 d\mu_1 + m'_2 d\mu_2 + \cdots + m'_n d\mu_n . \qquad (1)$$

In this equation p denotes the pressure, t the temperature, v', η' denote the volume and the entropy of the first phase, $\mu_1, \mu_2, \cdots \mu_n$ the chemical potentials of the n independent components of the system, and $m'_1, m'_2 \cdots m'_n$ the masses of these components contained in the first phase. For each of the r phases there is an equation similar to (1).

Let us denote by M_i the mass of the i-th phase, by v_i, η_i the volume and the entropy of the unit of mass of the i-th phase, by

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[1] On the Equilibrium of Heterogeneous Substances. Equations 129 and 132.

m_{ij} the mass of the j-th component which is contained in the unit of mass of the i-th phase, and by $\mathfrak{M}_j$ the total mass of the j-th component. Moreover, let us denote the volume and the entropy of the system by V and H.

If we divide the equation which corresponds to the i-th phase by M_i, and if we make use of the foregoing notation, we shall obtain:

$$v_i dp = \eta_i dt + m_{i1} d\mu_1 + m_{i2} d\mu_2 + \cdots + m_{in} d\mu_n , \qquad (2)$$
$$[i = 1,\ 2, \cdots r.$$

For univariant systems $r = n + 1$. Accordingly, in this case, we may eliminate the n quantities $d\mu_1$, $d\mu_2$, $\cdots d\mu_n$ from the $n + 1$ equations (2). We obtain in this way Gibbs's first equation:

$$\begin{vmatrix} v_1 & m_{11} & m_{12} & \cdots & m_{1n} \\ v_2 & m_{21} & m_{22} & \cdots & m_{2n} \\ \vdots & \vdots & \vdots & & \vdots \\ v_{n+1} & m_{n+11} & m_{n+12} & \cdots & m_{n+1n} \end{vmatrix} dp = \begin{vmatrix} \eta_1 & m_{11} & m_{12} & \cdots & m_{1n} \\ \eta_2 & m_{21} & m_{22} & \cdots & m_{2n} \\ \vdots & \vdots & \vdots & & \vdots \\ \eta_{n+1} & m_{n+11} & m_{n+12} & \cdots & m_{n+1n} \end{vmatrix} dt. \qquad (3)$$

Writing the equations which express the fact that the total mass of a component in the system is equal to the sum of the masses of this component in the different phases, we have the n equations:

$$M_1 m_{1j} + M_2 m_{2j} + \cdots + M_{n+1} m_{n+1j} = \mathfrak{M}_j, \quad [j = 1,\ 2, \cdots n. \qquad (4)$$

These n equations are not sufficient to determine the $n + 1$ quantities M_i. If we denote by M_i and M'_i two sets of solutions of equations (4), it follows that

$$(M'_1 - M_1) m_{1j} + (M'_2 - M_2) m_{2j} + \cdots + (M'_{n+1} - M_{n+1}) m_{n+1j} = 0,$$
$$[j = 1,\ 2, \cdots n. \qquad (5)$$

Moreover, if we denote the volume and the entropy corresponding to M'_i by V′ and H′ we have

$$M_1 v_1 + M_2 v_2 + \cdots + M_{n+1} v_{n+1} = V,$$
$$M'_1 v_1 + M'_2 v_2 + \cdots + M'_{n+1} v_{n+1} = V',$$

from which it follows immediately that

$$(M'_1 - M_1)v_1 + (M'_2 - M_2)v_2 + \cdots + (M'_{n+1} - M_{n+1})v_{n+1} = V' - V. \quad (6)$$

Similarly it can be shown that

$$(M'_1 - M_1)\eta_1 + (M'_2 - M_2)\eta_2 + \cdots + (M'_{n+1} - M_{n+1})\eta_{n+1} = H' - H. \quad (7)$$

Eliminating the $n + 1$ quantities $M'_i - M_i$ from the $n + 2$ equations (5), (6), (7), we find that

$$\begin{vmatrix} H' - H & V' - V & 0 & 0 & \cdots & 0 \\ \eta_1 & v_1 & m_{11} & m_{12} & \cdots & m_{1n} \\ \eta_2 & v_2 & m_{21} & m_{22} & \cdots & m_{2n} \\ \vdots & \vdots & \vdots & \vdots & & \vdots \\ \eta_{n+1} & v_{n+1} & m_{n+11} & m_{n+12} & \cdots & m_{n+1n} \end{vmatrix} = 0,$$

and this determinant when expanded gives

$$(H' - H)\begin{vmatrix} v_1 & m_{11} & m_{12} & \cdots & m_{1n} \\ v_2 & m_{21} & m_{22} & \cdots & m_{2n} \\ \vdots & \vdots & \vdots & & \vdots \\ v_{n+1} & m_{n+11} & m_{n+12} & \cdots & m_{n+1n} \end{vmatrix}$$

$$= (V' - V)\begin{vmatrix} \eta_1 & m_{11} & m_{12} & \cdots & m_{1n} \\ \eta_2 & m_{21} & m_{22} & \cdots & m_{2n} \\ \vdots & \vdots & \vdots & & \vdots \\ \eta_{n+1} & m_{n+11} & m_{n+12} & \cdots & m_{n+1n} \end{vmatrix}. \quad (8)$$

The comparison of equations (3) and (8) shows that

$$\frac{dp}{dt} = \frac{H' - H}{V' - V}, \quad (9)$$

and this equation takes the well-known form

$$\frac{dp}{dt} = \frac{Q}{t(V' - V)}, \quad (10)$$

if we denote by Q the quantity of heat which the univariant system absorbs in expanding from the volume V to the volume V' at the constant temperature t.

Next, suppose that the system considered is bivariant. In that case $r = n$, and accordingly from the n equations (2) we can eliminate $n - 1$ of the quantities $d\mu_j$, say $d\mu_2, d\mu_3, \ldots d\mu_n$. The result of the elimination is the second of Gibbs's equations:

$$\begin{vmatrix} v_1 & m_{12} & m_{13} & \cdots & m_{1n} \\ v_2 & m_{22} & m_{23} & \cdots & m_{2n} \\ \vdots & \vdots & \vdots & & \vdots \\ v_n & m_{n2} & m_{n3} & \cdots & m_{nn} \end{vmatrix} dp = \begin{vmatrix} \eta_1 & m_{12} & m_{13} & \cdots & m_{1n} \\ \eta_2 & m_{22} & m_{23} & \cdots & m_{2n} \\ \vdots & \vdots & \vdots & & \vdots \\ \eta_n & m_{n2} & m_{n3} & \cdots & m_{nn} \end{vmatrix} dt$$

$$+ \begin{vmatrix} m_{11} & m_{12} & \cdots & m_{1n} \\ m_{21} & m_{22} & \cdots & m_{2n} \\ \vdots & \vdots & & \vdots \\ m_{n1} & m_{n2} & \cdots & m_{nn} \end{vmatrix} d\mu_1. \qquad (11)$$

We shall now show that, if

$$\begin{vmatrix} m_{11} & m_{12} & \cdots & m_{1n} \\ m_{21} & m_{22} & \cdots & m_{2n} \\ \vdots & \vdots & & \vdots \\ m_{n1} & m_{n2} & \cdots & m_{nn} \end{vmatrix} = 0, \qquad (12)$$

equation (11) can be put into the form of the Clapeyron–Clausius equation.

When equation (12) is satisfied, the n equations

$$M_1 m_{1j} + M_2 m_{2j} + \cdots + M_n m_{nj} = \mathfrak{M}_j \quad [j = 1, 2, \ldots n. \qquad (13)$$

give infinite values for the quantities M_i, unless the following n conditions are also verified:

$$\begin{vmatrix} \mathfrak{M}_1 & m_{21} & m_{31} & \cdots & m_{n1} \\ \mathfrak{M}_2 & m_{22} & m_{32} & \cdots & m_{n2} \\ \vdots & \vdots & \vdots & & \vdots \\ \mathfrak{M}_n & m_{2n} & m_{3n} & \cdots & m_{nn} \end{vmatrix} = 0, \quad \begin{vmatrix} m_{11} & \mathfrak{M}_1 & m_{31} & \cdots & m_{n1} \\ m_{12} & \mathfrak{M}_2 & m_{32} & \cdots & m_{n2} \\ \vdots & \vdots & \vdots & & \vdots \\ m_{1n} & \mathfrak{M}_n & m_{3n} & \cdots & m_{nn} \end{vmatrix} = 0,$$

$$\cdots \begin{vmatrix} m_{11} & m_{21} & m_{31} & \cdots & \mathfrak{M}_1 \\ m_{12} & m_{22} & m_{32} & \cdots & \mathfrak{M}_2 \\ \vdots & \vdots & \vdots & & \vdots \\ m_{1n} & m_{2n} & m_{n3} & \cdots & \mathfrak{M}_n \end{vmatrix} = 0. \qquad (14)$$

These n homogeneous linear equations for the quantities $\mathfrak{M}_j$ are compatible. For if we form their discriminant it is at once apparent that the various terms in the resulting determinant are respectively the minors of the determinant of equation (12). The discriminant is thus a power of the determinant in equation (12), and it is accordingly equal to zero.

If we suppose that the masses $\mathfrak{M}_j$ have values which satisfy equations (14), the equations (13) are no longer sufficient to determine the masses M_i. We know, from the theory of linear equations, that we may replace one of the equations (13), say the first, by the equation

$$M_1 \begin{vmatrix} m_{11} & m_{21} & \cdots & m_{n1} \\ m_{12} & m_{22} & \cdots & m_{n2} \\ \vdots & \vdots & & \vdots \\ m_{1n} & m_{2n} & \cdots & m_{nn} \end{vmatrix} = \begin{vmatrix} \mathfrak{M}_1 & m_{21} & \cdots & m_{n1} \\ \mathfrak{M}_2 & m_{22} & \cdots & m_{n2} \\ \vdots & \vdots & & \vdots \\ \mathfrak{M}_n & m_{2n} & \cdots & m_{nn} \end{vmatrix}.$$

But as the determinants in this equation are equal to zero, M_1 may be chosen arbitrarily. The remaining $n - 1$ equations of the group (13) will then determine the $n - 1$ masses $M_2, M_3, \ldots M_n$. The first equation of the group (13) is thus a consequence of the others.

Thus, when equations (12) and (14) are verified, the bivariant system presents the following characteristics of a univariant system: the temperature and pressure are connected by an equation, equation (12), and the masses of the phases may vary while the pressure and temperature remain constant. The bivariant system is then said to be in an indifferent state.

If M'_i, M_i be two sets of solutions of equations (13), we have

$$(M'_1 - M_1)m_{1j} + (M'_2 - M_2)m_{2j} + \cdots + (M'_n - M_n)m_{nj} = 0, \qquad [j = 2, 3, \cdots n. \quad (15)$$

and also the following equations analogous to equations (6) and (7),

$$(M_1' - M_1)v_1 + (M_2' - M_2)v_2 + \cdots + (M_n' - M_n)v_n = V' - V, \quad (16)$$

$$(M_1' - M_1)\eta_1 + (M_2' - M_2)\eta_2 + \cdots + (M_n' - M_n)\eta_n = H' - H. \quad (17)$$

Eliminating the n quantities of $M_i' - M_i$ from the $n + 1$ equations (15), (16), and (17), we get

$$\begin{vmatrix} H' - H & V' - V & 0 & 0 & \cdots & 0 \\ \eta_1 & v_1 & m_{12} & m_{13} & \cdots & m_{1n} \\ \eta_2 & v_2 & m_{22} & m_{23} & \cdots & m_{2n} \\ \vdots & \vdots & \vdots & \vdots & & \vdots \\ \eta_n & v_n & m_{n2} & m_{n3} & \cdots & m_{nn} \end{vmatrix} = 0,$$

which, expanded, becomes

$$(H'-H) \begin{vmatrix} v_1 & m_{12} & m_{13} & \cdots & m_{1n} \\ v_2 & m_{22} & m_{23} & \cdots & m_{2n} \\ \vdots & \vdots & \vdots & & \vdots \\ v_n & m_{n2} & m_{n3} & \cdots & m_{nn} \end{vmatrix}$$

$$= (V'-V) \begin{vmatrix} \eta_1 & m_{12} & m_{13} & \cdots & m_{1n} \\ \eta_2 & m_{22} & m_{23} & \cdots & m_{2n} \\ \vdots & \vdots & \vdots & & \vdots \\ \eta_n & m_{n2} & m_{n3} & \cdots & m_{nn} \end{vmatrix}. \qquad (18)$$

The comparison of equations (18) and (11), in which the last term now disappears, shows that

$$\frac{dp}{dt} = \frac{H' - H}{V' - V}, \qquad (19)$$

or

$$\frac{dp}{dt} = \frac{Q}{t(V' - V)}, \qquad (20)$$

if we denote by Q the quantity of heat which the bivariant system in the indifferent state absorbs in expanding from the volume V to the volume V′ at the constant temperature t. This equation completes the analogy which exists between the behavior of a univariant system and the behavior of a bivariant system in an indifferent state.

In this connection, it is interesting to note that the demonstration which Clapeyron gives of his formula is as general as it is simple. His reasoning applies to any system of constant mass whose state is determined by its pressure and volume. But one of the consequences of the phase rule is that, with the one exception of invariant systems, the state of every system of constant mass is determined by its pressure and volume. The formula which we have established is thus a special case of Clapeyron's theorem, and as such cannot be called new; nevertheless it remained unnoticed until quite recently.

Bordeaux, January, 1900.

THE ELECTROLYSIS OF SODIUM CHLORIDE

BY C. G. L. WOLF

The electrolysis of alkaline chlorides has been examined by numerous observers, of whom Oettel[1] was the first perhaps to introduce quantitative methods into use, especially those which had to do with the examination of the gas produced at the electrodes. He also recognized the importance of the close observation of this part of the reaction. The usual procedure followed is to collect the gases and to compare them with the amount furnished by a gas voltameter in series, or to estimate the amount of current with a copper voltameter placed in a similar position in the circuit. This gives a relation between the amount of gas used up in the processes of reduction and oxidation, and the amount of gas which would be produced did neither of these reactions occur.

It has been usual to collect the combined gases, and by an analysis to determine the proportion of the oxygen and hydrogen in the mixture to one another. No attempt, however, has apparently been made to collect the gases separately.

As the recent work of Foerster[2] and Müller[3] has shown how important and instructive is the electrolysis of chlorides not only from a technical,[4] but also from a scientific standpoint, it has been thought worthy of attention that an apparatus should be constructed which should be available for the student. In the course of some work in this direction, which had as one of its aims the construction of an apparatus for class purposes, the following arrangement has been designed, which permits of the

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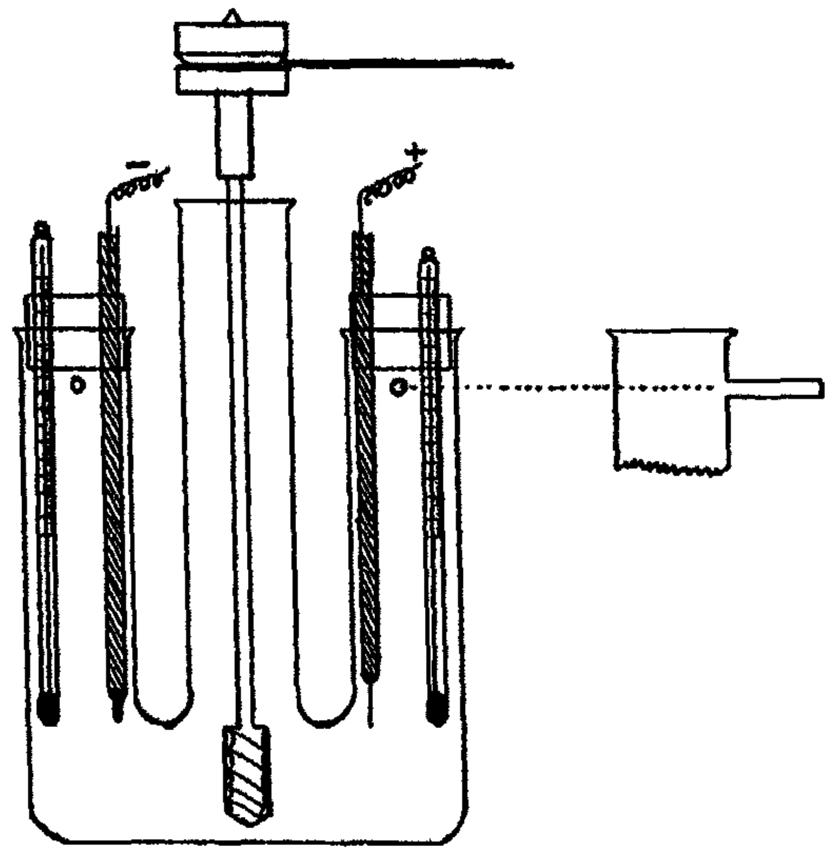
[1] Zeit. Elektrochemie, 1, 474 (1895).
[2] Zeit. anorg. Chem. 22, 1 (1899).
[3] Ibid. 22, 33 (1899).
[4] Kershaw. Elect. Review, 1898, 1096.

variation of conditions as quickly as possible and with a minimum of rearrangement. The apparatus can also be used for lecture demonstration, and the effect of alkalies, acids, or neutral salts on electrolysis can be shown without interrupting the current.

The main piece of apparatus consists of a U-tube with arms 10 cm long and 2 cm in width. Between the arms of the tube is sealed a third arm 15 cm in length. At right angles to the plane of the arm and 4 cm from the top are two small tubes for the delivery of the gases evolved. The mouth of each arm is closed with a doubly bored rubber stopper, which is provided with a thermometer and a glass tube carrying the electrode. Contact is made with the usual mercury connection. The mouth of the tube may be sealed with mercury to prevent the escape of gas through the rubber stopper. The small side tube for the delivery of the gas from each of the arms is joined to a three-way stop-cock by means of a stout piece of pressure tubing. The stop-cock is in turn connected with a Schiff's nitrometer.



In order to use the apparatus the measuring tubes of the nitrometers are filled with water by shutting off the connection between them and the electrolytic cell. Under these circumstances the cell communicates with the air. The reservoir of each eudiometer is lowered till the level of the water contained in it is about 0.5 cm above the lower opening of the small tube of the nitrometer. The stop-cock is now turned so that the levels in the reservoir and in the small tube are the same. On connecting the apparatus with the eudiometer by turning the stop-cock through 90° and starting the current, all the gas formed in the electrolysis is collected in the eudiometer.

It will be found that with a rapid evolution of gas a small amount of back pressure will be exerted in the cell, causing the liquid in the central tube to rise. This is obviated by lowering the levels of the eudiometer reservoirs a fraction of a centimeter, by which the original condition of the liquid in the cell is restored. This might also be done by running the shaft of the stirrer through a mercury seal, thereby completely closing the apparatus.[1]

When it is wished to stop the entrance of the gas into the nitrometer tubes, the stop-cocks are turned so that the cell now communicates with the outside air. The volume of the gases in the burettes is measured, the tubes again filled with water and the nitrometers are ready for the reception of gas.

The central tube of the electrolytic cell was provided with a small but efficient stirrer, run by an Ajax motor, and, as the results of experiments showed, this stirring had a marked effect on the progress of the oxidation. Especially in cases where the stirring was neglected or was performed inefficiently, a formation of bichromate took place around the anode. This was either due to the primary formation of hydrochloric acid in the electrolysis of the sodium chloride itself, which in turn acted on the chromate forming bichromate, or to the direct oxidation of the chromate itself. The appearance of the bichromate was much more marked where 1.8 percent of potassium chromate was present than where 1/10 of that amount was used.

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[1] Beckmann. Zeit. phys. Chem. 22, 616 (1897).

In any event the efficiency at the anode was lowered by the lack of a suitable stirring apparatus, and the inefficiency rapidly increased during the course of the experiment.

At low temperatures chlorine and oxides of chlorine were also given off. Both these phenomena disappeared or were diminished when the stirring was continued.

The cell itself was immersed in a water-bath kept at a fairly constant temperature by means of a small thermoregulator, the water was also stirred by means of a Witt stirrer.

The general arrangement of the apparatus for this preliminary work was that an oxy-hydrogen voltameter and a Weston ammeter were run in series with the cell.

By a suitable arrangement of commutators the current was passed through the cell, voltameter, and ammeter, or through the cell, ammeter, and a small open cell containing dilute sulphuric acid of the same resistance as the voltameter.

In this way the amount of current passing through the electrolytic cell was the same whether the voltameter was in a series or not. This arrangement also had the advantage that the current was in use continuously except for the fraction of a second necessary to commutate the switch.

The time during which the gas was collected was that necessary to give about 65 to 75 cc of electrolytic gas.

The temperature of the electrolyte was always some three degrees higher than that of the outer bath, owing to the heating effect of the current, but where the bath and the current were both regulated, a satisfactory degree of constancy could be obtained.

The current was furnished by a 100 volt dynamo circuit, which was cut down by a suitable arrangement of lamps. Fine regulation was made with a wire resistance. In these experiments the difference of potential at the two electrodes was not measured.

In a simple form of apparatus used by Mr. Pettit in this laboratory, the gases were delivered through a tube passed through the stopper and caught in inverted burettes standing in a pneumatic trough. This arrangement, although simpler, is not so convenient as the Schiff nitrometer, as the burettes must be transferred to a levelling trough in order to obtain the gas under atmospheric pressure.

The solution used was that of Müller containing 300 grams of sodium chloride and 1.8 grams of potassium chromate in 1000 cc. In Mr. Pettit's experiments a similar solution was used, but potassium chloride replaced the sodium salt. Under these conditions the difficultly soluble potassium chlorate crystallizes out. This does not happen when sodium chloride is used.

The following table gives the results of the electrolysis of 55 cc of the solution for 7 ampere hours. The anode was made from platinum foil, while the cathode consisted of a stout piece of platinum wire 1 mm in thickness.

TABLE I

300 grams NaCl. 1.8 grams K_2CrO_4 in 1000 cc. Current 1 ampere; $D_c = 6.66 \frac{\text{amp}}{\text{cm}^2}$; $D_a = 0.14 \frac{\text{amp}}{\text{cm}^2}$. Time 7 hrs 23 min.
Total current 7.38 ampere hours. Amount of solution 55 cc = 16.5 grams NaCl

Time	Amperes	Temperature	Percent inefficiency at cathode	Percent inefficiency at anode	Total efficiency
..	0.85	40.0	0.0	9.8	90.2
20′	1.00	42.0	0.5	14.5	85.0
47	1.02	42.5	1.1	19.4	79.5
79	1.09	43.0	0.0	21.1	78.9
131	1.00	43.2	0.9	21.7	77.4
229	1.01	42.8	1.4	18.4	80.2
249	1.00	42.0	0.9	19.3	79.8
313	0.90	40.2	0.2	17.8	82.0
379	0.90	40.2	0.9	19.8	79.3
429	0.99	41.2	1.3	19.6	78.1
443	1.00	41.0	1.0	19.4	79.6

As will be seen from the foregoing table, the mean current was about one ampere, and the total amount of current used was about 7.4 ampere hours. The amount of oxygen consumed in the oxidation should have been 15.9 percent of that required for the complete oxidation of the sodium chloride to sodium chlorate. As the average efficiency was about 80 percent, the amount of sodium chloride completely oxidized was about 12.7 percent. With this amount of oxidation the total efficiency of the apparatus was 79.6 percent at the end of the experiment. This result differs from that of Müller, whose efficiency in a run parallel with this in the matter of current used fell from 83.5 percent at the beginning to 67.5 percent at the end of the run. In this experiment Müller used 500 cc of the electrolyte. The solution was electrolyzed for 20 hours, 102.05 grams of copper being deposited by the voltameter. This amount of copper is equal to 25.75 grams of oxygen. As 500 cc of the solution contained 150 grams of sodium chloride which requires 124 grams of oxygen for complete oxidation to chlorate the reaction was 17.1 percent complete. The electrode densities used by Müller were: $D_a = 0.075 \frac{\text{amp}}{\text{cm}^2}$; $D_c = 0.18 \frac{\text{amp}}{\text{cm}^2}$. In the above table where 18.3 grams were electrolyzed the reaction was 12.7 percent complete.

In Mr. Pettit's experiments where the cathode density was $6.66 \frac{\text{amp}}{\text{cm}^2}$ and the anode density $0.22 \frac{\text{amp}}{\text{cm}^2}$, the current density at the former was 6.0 times that used by Müller, while the anode density was 28 times as great. In these experiments the total efficiency varied from 95 to 59 percent. This result compares favorably with that of Müller when the great difference in the densities is taken into account. In these experiments also the facilities for keeping the temperature constant were not so great as in later work.

In my own experiments with the same density at the cathode and a lower density at the anode, the efficiency was more constant, varying from 90.2 to 77.4 percent.

These experiments tend to show that this result is due largely to the efficient stirring and the improved means to secure constant temperature.

The apparatus would therefore appear to present several advantages over those which have been suggested, especially for demonstration purposes, viz.

I. The maintenance of a constant temperature.

II. It allows the introduction of thermometers at both electrodes.

III. The use of an efficient stirring apparatus during the electrolysis.

IV. The measurement of the evolved gases without the aid of a gas analysis.

V. The introduction of substances into the solution during the electrolysis without disarranging the apparatus.

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THE RELATION OF THE TASTE OF ACIDS TO THEIR DEGREE OF DISSOCIATION, II

BY THEODORE WILLIAM RICHARDS

Some years ago[1] it was shown that weak acids have a more strongly acid taste than is demanded by their degree of dissociation. In a recent interesting article upon the taste of acid salts, Kahlenberg[2] shows that these bodies also have a far stronger taste than one would expect.

Two possible explanations of these phenomena were given in the first paper:[3] either the act of tasting removes hydrogen ions and thus induces the formation of more, or else the undissociated acid possesses a taste similar to that of hydrogen ions. Kahlenberg ascribes the acid taste in his case to the anion (for instance HC_2O_4'), an interpretation which is impossible in the case of a monobasic acid, because the neutral salts in question are practically tasteless.

While it is undoubtedly true that many undissociated substances (for example sugar) have a strong taste, and that some anions also have a perceptible taste,[4] it seems to me probable that in the cases of the weak acids in question, the hydrogen ion is the

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[1] Richards. Am. Chem. Jour. 20, 121 (1898). Kastle. Ibid. 466. Kahlenberg. Jour. Phys. Chem. 3, 66 (1899); Zeit. phys. Chem. 29, 343 (1899). E. H. S. Bailey published in 1887 a brief note concerning the taste of acids, but since this was before the acceptance of the dissociation hypothesis, he was puzzled rather by the fact that acetic acid had not so strong a taste as hydrochloric acid than by the present question. (Proc. Kansas Acad. Sci. 11, 10.) This paper was known to none of the above authors at the time of writing, and my attention has been kindly called to it by Professor Bailey.

[2] Kahlenberg. Jour. Phys. Chem. 4, 33 (1900).

[3] Richards. Am. Chem. Jour. 20, 123 (1898).

[4] Höber und Kiesow. Zeit. phys. Chem. 27, 601 (1898). Kahlenberg. loc. cit.

chief agent, and hence that the first explanation is the true one.

The natural timidity felt by a chemist as regards even a limited excursion into the physiologist's domain, prevented me from offering any more definite hypothesis at the time, but the present occasion seems to warrant a further explanation. The fundamental cause of the sensation of taste is not yet clear; perhaps the most probable view is that the sensation is due to temporary chemical change in the tongue surface. It is clear that osmotic action alone cannot be the cause, for in that case all isotonic solutions should taste alike. The cell walls, it is true, may be permeable to some bodies and impermeable to others; but a cursory glance at the list of strong tasting substances seems to show that if such a partial permeability exists, it must depend upon physico-chemical and not upon purely physical characteristics of the dissolved substances.

Since the object of this paper is merely to show that the irregular phenomena manifested by the taste of acids may be explained in a physico-chemical fashion, the other possible hypotheses need not be considered here. We shall assume, then, that the phenomena of taste are due primarily to chemical reactions taking place in the tongue-surface, and seek to discover if the assumption leads us to inconsistencies as far as the taste of acids is concerned. It is quite possible that taste, like sight, is caused by only a few independent reactions;—that all the variety of tastes may be due simply to the superposition of these sensations, just as all the variety of colors is known to be due simply to violet, green and red.[1] The manufacture of scents from a combination of substances whose individual odors everyone condemns, is an analogous case illustrating this possibility. The existence of indol in the oil of jassamine is another similar case in point. It is well known, at least, that the number of true taste sensations is far fewer than is popularly supposed, for many of our so-called tastes are really smells.[2]

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[1] See for example "An American Text Book of Physiology." Howell, p. 851 (1896).

[2] Ramsay has published an interesting paper on the relation of smell to

However all this may be, it is certain that the sourness of acids is one of the simplest and most powerful of tastes, and hence one best adapted to furnish material for the consideration of the whole question. If we accept the theory of electrolytic dissociation, we cannot doubt that the taste of strong acids, much diluted with water, is due to the hydrogen ion; although the tastes of many other ions are so feeble that conclusions as regards origin of the peculiar tastes of salts are rather hazardous.

How then does the hydrogen ion effect the supposed chemical change causing the sour taste? There are of course two ways in which the acid may act:—either catalytically, or else by direct combination. If the action is catalytic, the change in the concentration of the hydrogen ion in the neighborhood of the nerve terminal during the reaction cannot be large, for any acid existing in the tongue-surface must be exceedingly weak. Hence taste should be a fairly accurate indicator of the concentration of the hydrogen ion. This assumption then leads us to a result in opposition to the facts; and in order to maintain it one must make the unlikely extra assumption that a complex body is capable of producing the simple effect caused by ionized hydrogen.

On the other hand, if, as seems more probable, the taste-reaction is one into which the hydrogen ion actually enters, such as the action of a strong acid on the salt of a weak one, or the neutralization of a nitrogenous organic base,[1] it is clear that the act of tasting must remove ionized hydrogen from the liquid tasted. The removal of this ion must of course upset the equilibrium, and immediately more of the acid which is being

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the chemical nature of the odoriferous body. A similar study of taste would be interesting also; — for example, a comparative study of the sweetness of polyatomic alcohols, or of the relative effect of the ketone and the aldehyde group in the sugars, etc. Professor Ramsay's paper was printed in the Proceedings of the Glasgow Phil. Soc. a number of years ago, and was partly reprinted in Nature, **26**, 187 (1882).

[1] An interesting paper by Bugarszky and Lieberman [Pflüger's Archiv. **72**, 51 (1898)] indicates a class of reactions which may be the important ones in this case. I am greatly indebted to Mr. L. J. Henderson, of the Harvard Medical School, for his kindness in preparing for me an abstract of this article.

tasted must be dissociated, according to the law of mass action. The newly ionized hydrogen must also be removed, allowing more to form, and so on. Hence a weak acid may cause a far greater change on the tongue-surface than corresponds to the concentration of the hydrogen ion in the pure acid; and *this* conclusion is wholly in accord with the facts.

Obviously, if acetic acid should yield up all its hydrogen ions to the tongue, it would taste as strong as an equivalent solution of hydrochloric acid. In such a case, one might as well attempt to determine the degree of dissociation by titration with baric hydroxide as by taste. The fact that weak acetic acid really tastes less sour than hydrochloric acid would tend to show that a state of equilibrium is reached before all the acetic acid has been dissociated; or else that the cell walls limit the speed of the reaction. The data are too inaccurate to make a quantitative calculation of value, but the principle involved is sufficiently evident. It is worthy of note that at least the order of sourness of weak acids is qualitatively correct, a fact which accords entirely with the present explanation.

Of course, precisely the same train of thought applies to weak acid salts; and indeed by analogy the explanation may be extended to the taste of hydroxyl ions. In this case quantitative measurement is even less certain because of the necessary presence of carbon dioxide. The explanation is in accord with the fact that hydrogen and hydroxyl ions possess a far stronger taste than most other ions; for it is obvious that these two should be more capable than any other ions of causing reactions in bodies likely to be present in the tongue-surface.

Physiologists have decided, I believe, that the different kinds of taste are perceived by different regions of the tongue. Of course the respective regions must be so constituted that the appropriate chemical reaction takes place near the nerve center fitted to receive the impulse. This fact may be used as an argument in favor of the present point of view; for unless there is some other disturbing factor, acid salts are said to be indistinguishable from pure acids by taste.

Of course other reactions, such as the formation of glucosides, must explain other tastes; but it is obvious that in these cases no such cumulative effect could be observed.

On the other hand, strong solutions of all kinds may easily exhaust from the tongue-surface itself the bodies capable of yielding the necessary reactions; hence the chemical explanation of taste elucidates also the partial paralysis of taste produced by concentrated solutions.

Thus none of the observed phenomena concerning the sour taste seem to be opposed to the hypothesis that weak acids and acid salts give a stronger taste than that which corresponds to their degree of ionization simply because hydrogen is deionized in the act of tasting. The other possible hypotheses of taste have not been disproved, because neither proof nor disproof is possible in the present state of our knowledge of physiological chemistry; but at least it has been shown that a satisfactory chemical theory of this particular taste is possible.

Harvard University, Cambridge, Mass., Feb. 14, 1900.

NEW BOOKS

Equilibre des Systèmes chimiques. *By J. Willard Gibbs. Translated by Henry Le Chatelier. (Bibliothèque de la Revue générale des Sciences.) 14 × 22 cm; pp. xii + 212. Paris: Carré et Naud. Price: cloth, 5 francs.*— The appearance of a carefully made and well printed French version of Gibbs's great paper on the Equilibrium of Heterogeneous Substances is to be hailed with pleasure; for the original in the Transactions of the Connecticut Academy is very expensive and otherwise inaccessible, and the only other separate print, Ostwald's German translation, is both badly printed and hard to read. In time, of course, a reprint in English of this remarkable work must appear; but, until that happy day arrives, the French translation will do very well. The world of physical chemistry owes Le Chatelier a debt of gratitude for his enterprise and well bestowed labor.

It should be pointed out that Le Chatelier's account, in his preface, of the published thermodynamic work of Gibbs is incomplete. He speaks only of the paper on the energy surface for one-component systems, and of the two parts of the great paper on the thermodynamic theory of chemical equilibrium. There are thus omitted from account, the paper, in the Trans. Conn. Acad., on thermodynamic plane diagrams, the paper of 1879, in the Am. Jour. Sci., on the theory of dissociation, and the British Association letters on electromotive forces. The present translation includes only the first half of the Equilibrium of Heterogeneous Systems; the latter half, on solids, the theory of capillarity, and electromotive forces, being omitted. Still, of the two, this portion of the work has the greater influence at the present time upon the development of both experimental and theoretical physical chemistry. Of his translation, Le Chatelier says:—

"The publication of this paper will remain an event of prime importance in the history of chemistry. H. Sainte-Claire Deville's discovery of dissociation, or, rather, of the reversibility of chemical phenomena, was not at first fully appreciated by chemists. They had been much more struck by the limitation of reactions than by their reversibility. The consequences of this reversibility, and, in particular, the possibility of applying to chemistry the principles of thermodynamics, had not been distinctly seen. Moutier and Peslin had pointed out merely that systems having a definite dissociation pressure must satisfy the Clapeyron formula. But to Gibbs is due the credit of having systematically applied the thermodynamic methods to create a new branch of chemical science, whose daily increasing importance has become comparable to that of the gravimetric chemistry created by Lavoisier."

J. E. Trevor

A Short History of the Progress of Scientific Chemistry in Our Own Times. *By William A. Tilden. 13 × 19 cm; pp. x + 276. New York: Longmans, Green, and Co., 1899. Price: cloth, $1.50.*—Tilden's little book is the outcome of a course of six popular lectures, on the history of chemistry, delivered in 1898 in a long established Course of Lectures to Working Men. The topics presented are briefly: The subject-matter of chemistry, the chemical elements, the combining weights of the elements, the periodic law, valence and constitution, synthetic chemistry, stereochemistry, the theory of solutions, and the liquefaction of gases. The book is short, is pleasingly and simply written, and is not too dogmatic. As a popular elementary presentation of its subject, it has distinct merits. *J. E. Trevor*

Grundriss einer Geschichte der Naturwissenschaften. *By Friedrich Dannemann. Vol. II. 14 × 22 cm; pp. 435. Leipzig: Wilhelm Engelmann, 1898. Price: paper 9, bound 10.50 marks.*—Dannemann's Outlines of a History of the Natural Sciences is a work in two volumes, of which the first gives a series of well-chosen selections from the publications which record the chief advances that have been made in the natural sciences, while the second presents a coherent outline of the whole development. Both volumes are well illustrated by cuts taken from the original sources. On the appearance of the first volume we referred with pleasure to its obvious merits; the second is now before us.

In this second volume the author arranges his material under four general heads: (1) Ancient Times, before the destruction of the Alexandrian Library in A.D. 642; (2) The Middle Ages, from A.D. 642 to the rise of the Copernican System; (3) Later Times, from Copernicus to the foundation of modern chemistry and the discovery of the voltaic cell; (4) The Present.

Under this fourth head we find, in order: the reformation of chemistry through the explanation of combustion and the discovery of the law of combining proportions; the discovery of the voltaic cell and the effects of the voltaic current; the development of theoretical and practical astronomy by Laplace and Herschel; the growth of physics and chemistry early in the century; zoology and botany; the natural sciences at the time of the discovery of the energy law; and the subsequent development of natural history, and of physics and chemistry.

The whole thing is written up in a clear and entertaining fashion, the philosophical aspect of the successive advances is kept well in the foreground, and the author has avoided the temptation to write too much. The result is emphatically a good and interesting book. *J. E. Trevor*

The Elements of Physics. *By Henry Crew. 13 × 19 cm; pp. xiii + 347. New York: The Macmillan Company, 1899. Price: cloth, $1.10.*—The author of this delightful little introductory treatise on physics has characterized it so well in his Preface, that we cannot give a better idea of his work than by quoting some of the remarks that he makes in his own behalf. He says that his confession of faith, in the matter of presenting elementary physics, is somewhat as follows:—

"1. Physics is not a series of disconnected subjects, including Mechanics, Sound, Light, Heat, and Electricity. It is, on the contrary, a body of well-organized truth, forming one great whole; illustrating, as do few other subjects, what Dickens called 'the universal dovetailedness of things.' It is, in fact, the science of matter and energy, the most fundamental of all the physical sciences, the foundation of nearly all branches of engineering.

"2. A science covering fields apparently so diverse, yet so intimately connected, demands an elementary treatment which shall be rigidly consecutive. When the student passes from Mechanics to Sound or from Heat to Electricity, he must not feel that he is taking up a new subject. If he does, something is wrong; and the chances are that his memory is being trained at the expense of his thinking power. Under such conditions he may learn many methods; he will hardly learn the one thing most to be desired, — method.

"Helmholtz, in his autobiographical sketch, makes one remark of especial significance to every instructor in elementary physics. Speaking of his early youth, he recalls that he met no difficulty in memorizing the poetry of the great masters because 'the flow of thought was natural'. Now physics, in too many of our schools, ranks as a most difficult subject. But dealing, as it does, with the familiar phenomena of daily life, and requiring, as it does, only a small fraction of the algebraic knowledge which the average student has already acquired, the author is inclined to believe that the difficulty lies chiefly in the presentation. If the presentation be smooth and if 'the flow of thought be natural', the elements of physics will not approach in difficulty the first few books of Euclid. ...

"3. An elementary presentation of physics should begin by resuming what might be called the experience of the average lad of sixteen years. The number of physical facts which a boy of this age has accumulated is astounding. Seldom, indeed, does the instructor appeal to him in vain for a verification of an elementary fact. The demand, therefore, is not so much for new facts, or for sheer facts of any kind, as for an orderly arrangement and an ability to use these facts.

"4. The author's experience is that secondary students find the use of algebraic language in the definition of physical quantities and sometimes in the description of physical facts exceedingly helpful, especially when the notation is well chosen. ... But let it not be forgotten that the algebraic definition should come last of all. First the idea must be acquired, then its description given in clear English, and *last of all*, in algebraic short-hand.

"5. The importance of limiting an elementary discussion of physics to matters that are really elementary and of avoiding mere descriptions of certain more or less ephemeral forms of apparatus cannot be overestimated.

"In the treatment of dynamics, however elementary, it is necessary to discuss many quantities which have direction as well as amount. If direction be an essential feature of velocity, momentum, force, etc.; if a twofold specification be necessary for these quantities while a single specification describes others; if all these directed quantities are added and subtracted according to the same rule; and if practically all students have observed the difference between these two kinds of quantities, it would seem helpful to employ the word *vector* to denote directed quantities, and *scalar* to denote others. These two names aid clear thinking and speaking concerning these two groups of quantities. ...

"6. Physics is an experimental science. Its foundations are experimental results. With rare exceptions, such as possibly Maxwell's *Electromagnetic Theory of Light*, all important contributions to the subject have been made through experiment. Experiment is the court of highest appeal in all physical results predicted by mathematical analysis. To attempt, therefore, to teach sound physics and good scientific method without laboratory work on the part of the student is to attempt the impossible. Accordingly the present volume is intended only for use in connection with a course of laboratory instruction."

The volume is a small one, wherefore the many trees do not hinder the student from seeing the wood. Yet, enough is told to give him a general idea of the subject, and it is told in a clear and thoroughly scientific way. The book could replace with advantage many an elementary college textbook now in use; and it is an admirable book to put into the hands of the serious general reader.

J. E. Trevor

De l'Influence de la Pression sur les Actions chimiques. *By Georges Aimé (1837). Avec une introduction par P. Duhem: La tension de dissociation avant H. Sainte-Claire Deville. 16 × 25 cm; pp. 32. Paris: A. Hermann, 1899.*—Some months ago (3, 364), there appeared in this Journal an article by P. Duhem, in which it was pointed out that the first clear formulation of the idea of dissociation pressure was presented by Georges Aimé in a Paris thesis printed in 1837. Thus was accorded recognition at a late day to the work of a man who advanced an important scientific idea before its time. In the pamphlet before us, Aimé's thesis is reprinted entire, with Duhem's article prefixed by way of introduction. Duhem has paused here to do the decent thing, and its doing gives one a thrill of real pleasure. *J. E. Trevor*

Lectures on Elementary Mathematics. *By Joseph Louis Lagrange. Translated by T. J. McCormack. 14 × 20 cm; pp. xiii + 156. Chicago: The Open Court Publishing Co., 1898. Price: cloth, $1.00.*—One of the many pleasing and useful recent publications of the Open Court Company is a translation, by Thomas J. McCormack, of Lagrange's Lectures on Elementary Mathematics. Mr. McCormack has appended to the translation an interesting biographical sketch of his author; and the volume is adorned by a beautiful engraved portrait of Lagrange. In his preface, Mr. McCormack says:—

"The present work, which is a translation of the *Leçons élémentaires sur les mathématiques* of Joseph Louis Lagrange, the greatest of modern analysts, and which is to be found in Volume VII. of the new edition of his collected works, consists of a series of lectures delivered in the year 1795 at the *Ecole Normale*,—an institution which was the direct outcome of the French Revolution and which gave the first impulse to modern practical ideals of education. . . .

"The originality, elegance, and symmetrical character of these lectures have been pointed out by De Morgan, and notably by Dühring, who places them in the front rank of elementary expositions, as an exemplar of their kind. Coming, as they do, from one of the greatest mathematicians of modern times, and with all the excellences which such a source implies, unique in their character as a *reading-book* in mathematics, and interwoven with historical and philosophical remarks of great helpfulness, they cannot fail to have a beneficent and stimulating influence."

J. E. Trevor

Leçons nouvelles sur les Applications géométriques du Calcul Différentiel. *By W. de Tannenberg. 17 × 25 cm; 192 pp. Paris: A. Hermann, 1899.*—Tannenberg's compact and clearly written little treatise is just the kind of thing that is needed for reference by the ordinary non-mathematician when studying the thermodynamic surfaces employed by Gibbs, and by van der Waals and others, or indeed when making use of any geometric representation in three coordinates. The chief methods of applying the differential calculus to the geometry of lines and surfaces are expounded in it under the five heads: Descriptive Properties of Lines; Descriptive Properties of Curved Surfaces; Metric Properties of Lines; Metric Properties of Ruled Surfaces; Metric Properties of Curved Surfaces. The book is an interesting indication of the present activity in scientific work at the University of Bordeaux, where its author is a professor of mathematics.

J. E. Trevor

Die Fortschritte der Physik. *Dargestellt von der physikalichen Gesellschaft zu Berlin. Im Jahre 1898. Erste Abtheilung: Physik der Materie; redigirt von Richard Börnstein. Pp. lxxvi + 694. Zweite Abtheilung: Physik des Aethers; redigirt von Richard Börnstein. Pp. liii + 984. 16 × 23 cm; Braunschweig: Friedr. Vieweg und Sohn, 1899. Price: paper, erste Abtheilung, 26 marks; zweite Abtheilung, 34 marks.*—Since our last announcement (3, 167), two more numbers of the *Fortschritte* have appeared,—the first two of the three for 1898. The first of these relates to the 'Physics of Matter', and includes all those branches of physics that do not fall under the heads light, heat, electricity, and astronomy. Physical chemistry is well represented, over half the work treated being physicochemical research in one form or another. The case is similar with the second section, which considers the work of the year in light, heat, and electricity. Under light, much chemical optics appears; while the work in theoretical and applied thermodynamics is almost all physical chemistry pure and simple. Much attention, of course, is given to electrochemistry. Altogether these volumes are as much a review of physicochemical research as they are anything else; and as such they are invaluable to the working physical chemist of either experimental or theoretical interests. The most of us do not need to be reminded of the high character and immense usefulness of this permanent work of reference.

J. E. Trevor

Harper's Scientific Memoirs. *No. 5. The Laws of Gases. Memoirs by Robert Boyle and E. H. Amagat. Translated and edited by Carl Barus. 107 pp. No. 6. The Second Law of Thermodynamics. Memoirs by Carnot, Clausius, and Thomson. Translated and edited by W. F. Magie. 151 pp. 13 × 20 cm; New York: American Book Company, 1889. Cloth.*—The latest numbers of Ames's series of Harper's Scientific Memoirs are little volumes entitled The Laws of Gases, and the Second Law of Thermodynamics. The former is edited by Carl Barus, and contains Boyle's 'A Defence of the Doctrine Touching the Spring and Weight of the Air' (London, 1662), Amagat's 'On the Compressibility of Gases at High Pressures' (Ann. Chim. Phys. (5) 22, 1881), parts of the same author's 'Memoir on the Elasticity and thermal Expansion of

Fluids throughout an Interval terminating in very high Pressures' (Ann. Chim. Phys. (6) 29, 1893), biographical sketches of Boyle and of Amagat, and a selected bibliography of the whole subject. The editor remarks: "Of course anybody may read the famous Memoirs of Amagat in the original; but everybody cannot so easily get these papers permanently into his possession. I believe, therefore, with the present translations to have scored a point in the interest of accessibility, and thus to have materially contributed to the advancement of science." All of which is undoubtedly true.

The other volume under notice is edited by W. F. Magie, and contains a translation of Carnot's paper (1824), a translation of Clausius's paper of 1850, selected portions of William Thomson's paper of 1851, 'On the Dynamical Theory of Heat', and biographical sketches of Carnot, Clausius, and Lord Kelvin. Both volumes are concerned with matters of the deepest physicochemical interest.

J. E. Trevor

Ostwald's Klassiker. *No. 104. Untersuchungen über die chemischen Affinitäten. By C. M. Guldberg and P. Waage. Translated and Edited by R. Abegg. pp. 182. Price: 3 marks. No. 109. Ueber die mathematische Theorie der electrodynamischen Induction. By R. Felici. Translated by B. Dessau; Edited by E. Wiedemann. pp. 121. Price, 1.80 marks. 12 × 19 cm; Leipzig: Wilhelm Engelmann.* — We have here two new volumes of Ostwald's *Klassiker* series. The first is a reprint of the famous Guldberg and Waage papers on the law of mass action. These comprise: a short paper, *Studien ueber die Affinität*, published in Norwegian in 1864; the big 'University Programme' of 1867, entitled *Untersuchungen ueber die chemischen Affinitäten*; and the familiar revision published in the Jour. prakt. Chem. in 1879 (and also in Norwegian in the same year) under the title *Ueber die chemische Affinität*. The volume is a valuable addition to the series, for the earlier papers have hitherto been practically inaccessible. It is edited and annotated by R. Abegg.

The other new volume presents a translation, from the Italian, of three papers by Felici on the theory of electrodynamic induction. It is translated by B. Dessau, of Bologna, and edited by E. Wiedemann.

J. E. Trevor

Science Abstracts. *Vol. III. Edited by W. R. Cooper. London, E. and F. N. Spon; New York, Spon and Chamberlain. Price, to non-members, $6.00 per year.* — Some time ago (2, 390), we had occasion to call attention to the admirable series of monthly reviews of the journal literature of physics (including physical chemistry) and electrical engineering, issued under the direction of the Institution of Electrical Engineers, and the Physical Society of London. With the beginning of the third volume, that for the present year, this journal is considerably enlarged, more especially in the consideration of steam plants, gas engines, oil engines, and motor cars.

The publication has shown itself to be a very useful one, its reviews being carefully prepared by a large staff of careful and conscientious abstractors. The scope of its work is indicated by the fact that in 1899 abstracts were made from 117 journals. The initial number of the new volume has 168 closely printed pages of reviews.

J. E. Trevor

A Treatise on Crystallography. *By W. J. Lewis. 15 × 22 cm; pp. viii + 612. (The Cambridge University Press), New York, the Macmillan Co., 1899. Price: cloth, $3.50, net.* — Unlike the works of Groth and Mallard, the 'Treatise' of Prof. Lewis is devoted almost exclusively to the geometrical side of crystallography; though there is a short chapter (pp. 138-147) on "the systems and some of the physical characters associated with them", and, in the sections in which the systems are severally described, the importance of their physical properties in classifying various minerals is thoroughly illustrated.

Throughout the work, Miller's notation and geometrical method are adopted, the elements of symmetry being discussed as though crystals were merely polyhedra with faces subject to the law of rational indices. This method has the advantage of being remarkably free from hypotheses, but fails to establish some of the observed properties of the triad axis (p. 114) which may be accounted for by the assumption of uniformity of internal structure in crystals. The author, however, enters into this question only far enough to show the inadmissibility of pentad axes and of axes of symmetry of higher degree than six (pp. 134-137).

Great stress is laid on the methods of drawing crystals. Not only are there chapters aggregating forty pages on planes and elevations, orthographic and clinographic drawings, and linear and stereographic projection; but throughout the book there are very numerous examples of the application of these methods to special cases, with hints on the judicious selection of the axial and parametral planes, of the angles to be measured, and of the forms to be drawn first. There can be no doubt that the student would gain far more from a careful study of a number of these special cases, — crystal, treatise, and drawing board at hand, — than from the same amount of time spent in poring over a collection of models, or of minerals. The mathematical knowledge presupposed is small, analytical methods having been almost completely excluded; and the practice in mechanical drawing would be of very decided advantage to most students of 'pure' science, whose education in that respect is so markedly inferior to that of the engineers.

The Treatise is illustrated by 553 clear-cut figures. A short descriptive chapter on goniometers, and an index of sixteen columns, close the work.

W. Lash Miller

Le Mois scientifique et industriel. *16 × 24 cm. 33 Bd. des Batignolles, Paris. Price, for foreign countries, 20 francs per year.* — Our attention is called to a new series of reviews of current progress in technical work, and in those lines of physical and chemical research that have an immediate technical bearing. Electricity, construction, lighting, photography, locomotion, metallurgy, and agriculture, with a little physics and chemistry, appear to be the chief departments that are considered.

J. E. Trevor

REVIEWS

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

General

On the absolute measure of time, deduced from the laws of attraction. *G. Lippmann. Comptes rendus*, 128, *1137* (*1899*). — "The numerical value of the Newtonian constant is independent of the choice of the units of length and mass; it depends solely on the choice of the unit of time. Conversely, the value of the interval of time taken as the unit is definitely determined if we give it the numerical value of the Newtonian constant which corresponds to it". There are then 3862 seconds in the absolute unit of time. *W. D. B.*

Determination of the atomic weight of boron. *H. Gautier. Comptes rendus*, 129, 595; *Ann. Chim. Phys.* (*7*) 18, *382* (*1899*). — The substances taken for analysis were the sulfid, chlorid, bromid, and carbid of boron. The values for boron obtained from these four compounds are 11.041, 11.021, 11.011, 10.997 respectively. The values selected by the author as the most probable is 11.016, the mean of the values for the chlorid and the bromid. *W. D. B.*

On the ratio of the atomic weights of oxygen and hydrogen. *A. Leduc. Comptes rendus*, 128, *1158* (*1899*). — The author points out that if one takes into account the expansion noticed by Sacerdote and Berthelot, the ratio of the atomic weight of oxygen to that of hydrogen becomes 15.878. *W. D. B.*

On the heat of formation of quick-lime. *H. Moissan. Comptes rendus*, 128, *384* (*1899*). — The value found is 145 Cal. *W. D. B.*

On double cyanids. *M. Berthelot. Comptes rendus*, 128, *630*, *706*; *Ann. Chim. Phys.* (*7*) 17, *451*, *453*, *456*, *470* (*1899*). — Thermochemical data. *W. D. B.*

New investigations on the heat of formation of various nitrogen compounds. *M. Berthelot and G. André. Comptes rendus*, 128, *959*; *Ann. Chim. Phys.* (*7*) 17, *433* (*1899*). — Thermochemical data. *W. D. B.*

Morphin and its salts. *E. Leroy. Comptes rendus*, 128, *1107* (*1899*). — Thermochemical data. *W. D. B.*

Heat of oxidation of sodium. *de Forcrand. Comptes rendus*, 128, *1449*, *1519* (*1899*). — Thermochemical data and conclusions from them. *W. D. B.*

Study of some basic or ammoniacal halid compounds of the metals. *E. Tassilly. Ann. Chim. Phys.* (*7*) 17, *38* (*1899*). — Thermochemical data. *W. D. B.*

Studies on polymerization. *P. Lemoult. Ann. Chim. Phys.* (*7*) 16, *338* (*1899*). — The title is misleading. The paper consists chiefly of thermochemical measurements on cyanic and cyanuric compounds. *W. D. B.*

One-Component Systems

On the boiling-point of liquid hydrogen under reduced pressure. *J. Dewar. Proc. Roy. Soc.* 64, *227*; *Ann. Chim. Phys.* (*7*) 17, *5* (*1899*). — Lowering the pressure under which liquid hydrogen boiled, from one atmosphere to 25 mm produced a change of only one degree in the boiling-point as registered on a platinum thermometer. The reason for this anomalous result has not yet been made out. *W. D. B.*

Studies on the vapors given off by the two forms of mercuric iodid. *D. Gernez. Comptes rendus*, 128, *1516* (*1899*). — In all sublimation experiments with mercuric iodid, the vapor condenses as yellow crystals whether one starts from the red or the yellow modification, and whether the temperature be below or above the transformation temperature. According to Ostwald's hypothesis the vapor should condense to the red form above 128°. *W. D. B.*

Some applications of molecular volumes. *A. Leduc. Comptes rendus*, 128, *1314*; *Ann. Chim. Phys.* (*7*) 17, *173* (*1899*). — The author writes the gas law in the form $pv = \phi r T$, where ϕ is called the "molecular volume" and is deduced from the critical data. This formula is applied fairly successfully to Ramsay and Young's measurements with ether, and to Young's measurements with isopentane. By taking this factor ϕ into account, it appears that the alleged dissociation of chlorin at high temperatures does not occur (3, 115). It is then pointed out that E. and L. Natanson were not justified in taking the so-called theoretical density of nitrogen peroxid when applying the formula of Gibbs to their data. Making the correction we get more satisfactory results at constant temperature, but the change of dissociation with the temperature still presents difficulties. There is also a discussion of the vapor-density of acetic acid with reference to Raoult's freezing-point measurements. This discussion would have been more valuable if van 't Hoff had not straightened the matter out years ago. *W. D. B.*

On the experiment of Lord Kelvin and Joule. *A. Leduc. Comptes rendus*, 128, *89* (*1899*). — A discussion of the experiment of Thomson and Joule, in which it is shown that the condition $dU/dV = 0$ is not sufficient in defining an ideal gas. *W. D. B.*

On the coefficient of expansion, characteristic of ideal gases. *D. Berthelot. Comptes rendus*, 128, *498* (*1899*). — The author claims that the most accurate measurements of the coefficient of expansion of gases point to −273° ± 0.1 as the starting-point of our temperature scale, rather than to −274° as has recently been claimed. *W. D. B.*

Note on the densities of "atmospheric nitrogen," pure nitrogen and argon. *W. Ramsay. Proc. Roy. Soc.* 64, *181* (*1898*). — It is pointed out that the data of Leduc and Schloesing agree as well as could be expected with those of Rayleigh, Ramsay, and Kellar, and "that the density of 'atmospheric nitrogen' is correctly given as the mean of the densities of the constituents, taken in the proportion in which they occur."

W. D. B.

The preparation and some of the properties of pure argon. *W. Ramsay and M. W. Travers. Proc. Roy. Soc.* 64, *183*; *Zeit. phys. Chem.* 28, *241* (*1899*). — To get pure argon, 1500 liters of atmospheric air were treated with metallic copper to remove the oxygen; with metallic magnesium to remove most of the nitrogen; with anhydrous lime and magnesium powder, and with copper oxid to remove the residual nitrogen and the hydrogen. The fifteen liters of argon were condensed to a liquid and subjected to fractional distillation to remove the neon, helium, and metargon. The amounts of krypton and xenon were too minute to be detected. The argon was then sparked with oxygen over caustic potash to remove any nitrogen that might still be present. The density of the purified argon is 19.957; the refractivity is 0.9665; there is no evidence of polymerization at the boiling-point of oxygen.

W. D. B.

Experiment on a new form of the function $f(p, v, t) = 0$ with reference to liquids. *E. H. Amagat. Comptes rendus,* 128, *538*, *649* (*1899*). — The author has previously suggested the formula

$$(p - P)(v - a) = RT,$$

where P is the internal pressure. On the basis of certain assumptions as to the form of the function

$$P = f(p, v, t)$$

the author deduces a very complicated formula which represents satisfactorily the experimental data for carbonic acid.

W. D. B.

On the relation between the molecular weight and the density of liquids. *D. Berthelot. Comptes rendus,* 128, *553*, *606*, (*1899*).—The author points out that it should be possible to calculate the molecular weight of a liquid from its density and the critical data. He then deduces the formula

$$M = 11.4\,d\,\frac{T_c}{p_c\left(2 - \frac{T}{T_c}\right)}$$

where p_c and T_c are the critical pressure and temperature and d is the density at the temperature T. This formula was then applied to forty-seven substances and in only five cases was there evidence of polymerization. The five exceptions were: acetic acid, methyl alcohol, ethyl alcohol, propyl alcohol, water.

W. D. B.

Some properties of aluminum. *A. Ditte. Comptes rendus,* 128, *195*; *Ann. Chim. Phys.* (7) 16, *162*; 17, *145* (*1899*). — In acid solutions aluminum rapidly becomes coated with a film of hydroxid which protects it from further attack. The combined effect of salt solutions, air and carbonic acid is first to produce gelatinous alumina and then the crystallized hydroxid, which latter does not protect the metal.

W. D. B.

On the impurities of aluminum. *A. Minet. Comptes rendus*, 128, *1163* (*1899*). — The aluminum of to-day contains about 0.15 percent of impurities, chiefly iron from the iron vessel in which the double fluorid is decomposed. The author proposes to eliminate this in one of two ways. Either to make the vessel a second cathode through which a small percentage of the current passes, thus coating the walls with aluminum; or to cover the walls thickly with carbon and to isolate the containing vessel completely from the electrodes.

W. D. B.

The specific heat of gases and the mechanical equivalent of the calorie. *A. Leduc. Ann. Chim. Phys.* (*7*) 17, *484* (*1899*). — This paper sums, in a connected whole, the substance of a number of short articles which have appeared in the Comptes rendus and which have been reviewed from that source.

W. D. B.

On copper reduced at low temperature. *A. Colson. Comptes rendus*, 128, *1458* (*1899*). — The author shows that the apparent difference in the properties of copper, when obtained by reduction above or below 200°, is due to the state of division. *W. D. B.*

A study of glucinum and its compounds. *P. Lebeau. Ann. Chim. Phys.* (*7*) 16, *457* (*1899*). — Glucinum oxid was melted by heating in the electric furnace. It is white, scratches quartz readily, and ruby but slightly; its density is 3.015. The chlorid, bromid, iodid, fluorid, and carbid of glucinum were also prepared and described. The metal was obtained by the electrolysis of the mixed fluorids of glucinum and potassium. Its density is 1.73 at 15°. A number of alloys were also prepared. *W. D. B.*

Studies on calcium and its compounds. *H. Moissan. Ann. Chim. Phys.* (*7*) 18, *289* (*1899*). — Reviewed (3, 413) from Comptes rendus, 126, 1753; 127, 584, 917 (1898).

Study of the latent heat of vaporization of piperidin, pyridin, acetonitrile, and capronitrile. *W. Louguinine. Comptes rendus*, 128, *366* (*1899*). — The molecular heats of vaporization divided by the absolute temperature are very nearly constant for these four substances. *W. D. B.*

On the heat conductivity of liquids. *E. van Aubel. Zeit. phys. Chem.* 28, *336* (*1899*). — Attention is called, without comment, to the fact that the recently published data of Lees do not agree with those obtained by others, and that they do not confirm the law of H. F. Weber. *W. D. B.*

Rapid method for determining the specific heats of liquids. *D. Negreano. Comptes rendus*, 128, *875* (*1899*). — "The principle of the method consists in the comparison of the times necessary to raise the temperature of equal volumes of water and any liquid whatsoever an equal number of degrees when the two liquids are heated by the same electric current." The novelty of the method lies in the assumption that the water-equivalent of the containing vessel and thermometer may be neglected. *W. D. B.*

Two-Component Systems

On the effects of various solvents on the allotropic change of mercuric iodide. *J. H. Kastle and M. E. Clark. Am. Chem. Jour.* 22, *473* (*1899*).—The authors show that practically all solutions of mercuric iodid are yellow in color and that the yellow form crystallizes first from all solutions. They conclude, apparently correctly, that dissolved mercuric iodid is yellow mercuric iodid, and not simply mercuric iodid. The paper is an interesting and valuable one, though it would have been more interesting and more valuable had the authors kept their solutions occasionally at constant temperature and had they made some observations on the inversion temperature. They have, however, furnished additional proof of the fact that the rate of change of one solid modification into another is affected enormously by the nature of the solvent. The supposition that red and yellow mercuric iodid can exist simultaneously in equilibrium with amyl alcohol at different temperatures is certainly erroneous; temperature fluctuations are unquestionably the disturbing factor. It is to be hoped that we may have another paper before long showing whether the inversion temperature is or is not changed by the solvent. *W. D. B.*

On the freezing-points of mixtures of acetic acid and water, and on the mutual solubility of these two substances. *L. C. de Coppet. Ann. Chim. Phys.* (7) 16, *275* (*1899*).—The complete freezing-point diagram for acetic acid and water has been determined. The eutectic point occurs at about –26.7°, the solution containing forty percent of water in grams. Owing to the ease of superfusion, both curves can be followed beyond the intersection point and the author puts but does not answer the question, how far is it possible theoretically to follow these curves. *W. D. B.*

On the freezing-points of mixtures of acetic acid and water. *C. Dahms. Ann. Chim. Phys.* (7) 18, *140* (*1899*).—It is claimed that experiments similar to those of de Coppet (preceding review) have already been published by the author (1, 377). *W. D. B.*

Reply to the note of Mr. A. Dahms. *L. C. de Coppet. Ann. Chim. Phys.* (7) 18, *142* (*1899*).—It has been pointed out that the author has determined freezing-points beyond the eutectic point, and that Dahms has not called attention to the fact that one and the same mixture may have a stable freezing-point above the eutectic temperature, and an instable one below the eutectic temperature. *W. D. B.*

The accurate determination of freezing-points and some applications to aqueous solutions. *F. M. Raoult. Ann. Chim. Phys.* (7) 16, *162* (*1899*).—Reviewed (3, 414) from Zeit. phys. Chem. 27, 617 (1898).

On the solubility in water of the normal acids of the oxalic acid type. *F. Lamoureux. Comptes rendus*, 128, *998* (*1899*).—The author shows that the remarkable law of alternating solubilities propounded by Henry is due to the abnormal behavior of malonic and glutaric acids, the acids with seven, nine, and eleven of carbon behaving as one would expect them to. *W. D. B.*

On the solubility of the substituted malonic acids. *G. Massol and F. Lamoureux. Comptes rendus,* 128, *1000* (*1899*).—The substituted malonic acids are more soluble in water than the corresponding acids of the oxalic acid series with the corresponding amount of carbon. *W. D. B.*

On the dissociation of mercuric oxid. *H. Pélabon. Comptes rendus,* 128, *825* (*1899*).—The author shows first that the oxygen pressure in the system liquid mercury, mercuric oxid, and oxygen, is a function of the temperature only, and can be represented by the formula

$$\log_{10} p = \frac{m}{T} + n \log T + z.$$

When no liquid mercury is present, the product of the oxygen pressure into the square of the mercury pressure is a function of the temperature only.

W. D. B.

On the suboxid of silver. *Guntz. Comptes rendus,* 128, *997* (*1899*).—The author finds that the dissociation pressure of Ag_4O is about 49 atms at 358°. By placing metallic silver in one tube and silver oxid in another, and exposing both to an oxygen pressure of about fifty atmospheres at 358°, the author succeeded in showing that the silver oxid lost half its oxygen while the metallic silver took up oxygen in the ratio of 1 O : 4 Ag. *W. D. B.*

On the decomposition of carbonic acid in presence of carbon. *O. Boudouard. Comptes rendus,* 18, *824, 1524* (*1899*).—At 650° the reaction between carbonic acid and carbon is reversible.

$$CO_2 + C \rightleftharpoons 2CO.$$

Equilibrium is reached when there is 61 percent of CO_2 and 39 percent of CO in the gaseous mixture. At 800° the mixture in equilibrium contains 93 percent of CO and 96 percent at 925°. *W. D. B.*

On van 't Hoff's equation and the molecular weights of liquids. *C. L. Speyers. Jour. Am. Chem. Soc.* 21, *725* (*1899*).—The point is made that the formula $\frac{n}{N+n} = \frac{p-p'}{p}$ does agree with the experimental facts and that the van 't Hoff formula $\frac{n}{N} = \log \frac{p}{p_1}$ does not. It is therefore proposed to take the first formula as the accurate one, N referring to the molecular weight of the solvent in the liquid and not in the vapor. A deduction of the van 't Hoff formula is given in which it is shown that the heat of dilution does not affect the results. The mistake here is that the author does not express his heat terms in work units. The amount of work necessary to condense a given amount of vapor to liquid is a function of the pressure, but not of the heat of vaporization. On the other hand, the work done in driving out N/*n* reacting weights of the solvent cannot be set equal to RT unless the heat of dilution is not zero, because that is one condition for which PV = RT.

While the mathematical reasoning is faulty, the fact remains that, in certain cases, the empirical formula does give better results than the other. Part of this is unquestionably due to experimental error. An error of one percent in grams in the composition of the vapor usually means more than that in percentage reacting weights. In concentrated solutions, one percent in the total vapor composition will mean anything from ten percent upward in the partial pressure with an enormous error in the calculated molecular weight. If the theoretical formula will not represent the facts, it must be given up, but the author has not yet proved his point. *W. D. B.*

Preparation and properties of lithium monomethylamin. *H. Moissan. Comptes rendus*, **128**, *26* (*1899*). — Lithium dissolves in methylamin forming a blue solution from which a solid compound $LiCH_3NH_2$ can be made to crystallize. At ordinary temperatures, the dissociation pressure is less than the atmospheric. *W. D. B.*

On the mixture of gases and the compressibility of gaseous mixtures. *D. Berthelot and P. Sacerdote. Comptes rendus*, **128**, *820* (*1899*).— Mixtures of CO_2 and SO_2 and of hydrogen and oxygen are less compressible than one would expect from the properties of the single gases, while no such differences can be detected with a mixture of oxygen and nitrogen. *W. D. B.*

On the increase of pressure caused by the mixture of two gases and on the compressibility of the mixture. *D. Berthelot. Comptes rendus*, **128**, *1159, 1229* (*1899*). — The author shows that the method of calculation suggested by him (3, 416) gives results agreeing well with those found experimentally by Sacerdote and Berthelot (preceding review). *W. D. B.*

On the temperature of maximum density of aqueous solutions of the alkaline chlorids. *L. C. de Coppet. Comptes rendus*, **128**, *1559* (*1899*). — The lowering of the temperature of maximum density of water is proportional to the concentration of the chlorids of potassium, sodium, lithium, and rubidium. The molecular lowering is only half as great for lithium chlorid as for any one of the other three salts. The temperature corresponding to the maximum density was determined from a study of instantaneous photographs of the solution. *W. D. B.*

On the dilution law of the electrolytes. *P. T. Müller. Comptes rendus*, **128**, *505* (*1899*).—It is claimed that the conductivity of salts as given by Kohlrausch can be represented by the formula

$$\mu = \mu_{\infty} \frac{-52.72}{V^{0.41504}}.$$

To represent Bredig's results 62.152 must be substituted for 52.72. *W. D. B.*

On the expansion of metallic alloys. *H. Le Chatelier. Comptes rendus*, **128**, *1444* (*1899*). — Some years ago when studying the freezing-point curves for binary alloys, the author obtained maximum freezing-points in certain cases for concentrations which did not correspond to any simple compound. As this pointed to the existence of solid solutions, the author has now studied the expansion of these same alloys. The maximum in the copper-antimony curve and one of the maxima in the copper-aluminum curve are thus shown to be due to solid solutions. *W. D. B.*

On the use of chlorate of potash in explosives containing ammonium nitrate. *H. Le Chatelier. Comptes rendus*, **128**, *1394* (*1899*). — Explosives containing ammonium nitrate are very useful in mines, but they do not always go off. The addition of potassium chlorate would obviate this difficulty, but might introduce others. It so happens, however, that potassium chlorate and ammonium nitrate form two series of solid solutions. It is therefore possible to prepare ammonium nitrate containing definite quantities of potassium chlorate as an isomorphous mixture. *W. D. B.*

Mixed compounds of phenyl hydrazin and another organic base with metallic salts. *J. Moitessier. Comptes rendus*, 128, *1336* (*1899*).—The author has prepared compounds containing anilin, phenyl hydrazin, and either zinc iodid, zinc bromid, nickel sulfate, or cadmium nitrate. In the case of zinc iodid, α-naphthylamin and β-naphthylamin have been substituted for anilin. *W. D. B.*

The variation of entropy during the dissociation of similar heterogeneous systems. *C. Matignon. Comptes rendus*, 128, *103* (*1899*). — The author shows that when the ammoniacal chlorids dissociate, the heat of reaction divided by the temperature at which the dissociation pressure equals the atmospheric pressure is a constant, or the change of the entropy is the same for all these compounds when dissociating under constant pressure. *W. D. B.*

On the thermal properties of lime prepared at different temperatures. *H. Gautier. Comptes rendus*, 128, *937* (*1899*).—The rate of hydration of lime varies enormously with the temperature to which the lime has previously been raised. Thinking that this might be due to polymerization, the author has determined the heat effect when hydrochloric acid solutions acted on limes that had been heated to 1000°, 1200°, 2000°, and above the melting-point. The values from the four experiments were identical. *W. D. B.*

Poly-Component Systems

Investigations on the dissociations of different ammoniacal compounds in the presence of water. *R. Jarry. Ann. Chim. Phys.* (7) 17, *327*, (*1899*).—The author has determined the dissociation pressures of the compounds of silver chlorid, bromid, and iodid, with ammonia, and with methyl amin by themselves, and in presence of water. He has also determined the solubility in aqueous solutions so far as possible, and has discussed the conditions for obtaining the different compounds in crystalline form. The dissociation pressures at zero in presence of water are practically equal to the sum of the dissociation pressures of the ammoniacal compound plus the vapor-pressure of pure water at that temperature. With the ammoniacal silver chlorids, the observed value is slightly higher than the sum of the single values which is the more surprising since the presence of the ammonia must reduce the partial pressure of the water. While the discrepancy is probably due to experimental error, it is unfortunate that the author should not have discussed this point more fully. *W. D. B*

The effect of di-ionic electrolytes on the solubility of the tri-ionic electrolytes with different ions. *A. A. Noyes and E. S. Chapin. Jour. Am. Chem. Soc.* 21, *511* (*1899*). — Reviewed (4, 53) from Zeit. phys. Chem. 28, 518 (1899).

On some abnormal freezing-point lowerings produced by chlorides and bromides of the alkaline earths. *H. C. Jones and S. J. Chambers. Am. Chem. Jour.* 23, *89* (*1900*). — It was found that the molecular lowering of the freezing-point passes through a minimum with increasing concentration at about 0.1 normal, in the case of the chlorids and bromids of the alkaline earths. No corresponding irregularity could be detected in the conductivity curves. As a provisional hypothesis to explain the anomalous results, the authors assume the existence of hydrates in solution. In the more concentrated solutions, the difference between the water actually present as solvent and the total water in the solution would cause a variation in the observed direction. [Heat effects should also be taken into account.] *W. D. B.*

Contributions to our knowledge of aqueous solutions of double salts, II. *H. C. Jones and K. Ota. Am. Chem. Jour.* 22, *5* (*1899*). — The authors have compared the conductivities of the double chlorids of potassium and zinc, potassium and cadmium, sodium and aluminum, ammonium and mercury, with the corresponding conductivities of the single salts. Except in the case of very dilute solutions, the conductivities for the double salts are much less than the sum of the conductivities for the single salts. The authors therefore consider the existence in solution of a certain proportion of double salt as proved. The variation from the sum of the conductivities is much greater with the chlorids than with the sulfates previously studied (1, 452). *W. D. B.*

The origin of the gases evolved on heating mineral substances, meteorites, etc. *M. W. Travers. Proc. Roy. Soc.* 64, *130* (*1898*). — It is shown that hydrogen and carbon monoxid are formed by a secondary reaction in many cases, in which these gases are obtained by heating minerals. The supposed presence of nitrogen in meteorites is attributed by the author to experimental error in the analysis. He points out further that only one-half the helium can be obtained from cleveite by heating and about the same proportion from fergusonite. From these experiments the following interesting conclusion is drawn :

"In the majority of cases where a mineral substance evolves gas under the influence of heat, the gas is the product of the decomposition or interaction of its non-gaseous constituents at the moment of the experiment. The results of such experiments cannot, therefore, serve as basis for speculation as to origin and history of the substances in question." *W. D. B.*

Displacement of mercury by hydrogen. *A. Colson. Comptes rendus,* 128, *1104* (*1899*). — The author has studied at 100° the reaction

$$HgO + H_2 = H_2O + Hg.$$

The rate of absorption of hydrogen is proportional to the mass of the mercuric oxid and to the cube root of the hydrogen pressure. The yellow oxid of mercury absorbs hydrogen five times as rapidly as the red modification. Hydrogen scarcely acts at all at 100° upon mercurous oxid, or mercuric chlorid. It reduces mercuric nitrate to mercuric oxid, nitric oxid, and water. *W. D. B.*

The theory of the formation of nickel sulphide. *J. L. R. Morgan and A. H. Gotthelf. Jour. Am. Chem. Soc.* 21, *494* (*1899*). — The point made is that the concentration of sulfid as ion in a solution saturated with nickel sulfid is so

nearly that of a solution saturated with hydrogen sulfid gas, that equilibrium is not reached within a conveniently measurable time. The idea is ingenious and deserving of credit; but it does not seem to be so simple nor to explain the facts so well as Ostwald's hypothesis of a change in the precipitated nickel sulfid. This hypothesis gives us indefinite leeway in regard to strength of acid and is perfectly compatible with the results quoted by the authors from Baubigny.
W. D. B.

The theory of the separation of barium, strontium, and calcium from the mixed sulphates. *J. L. R. Morgan. Jour. Am. Chem. Soc.* **21**, *522* (*1899*). — The author explains the action of ammonium carbonate on strontium and calcium sulfates by means of the 'solubility products' and shows, by the same course of reasoning, that barium sulfate will be decomposed only when the ratio of carbonate as ion to sulfate as ion in the solution exceeds 105 : 1. It is stated that neglecting hydrolysis produces no serious error, but this has since been disputed by Küster (next review). *W. D. B.*

On the separation of barium, strontium, and calcium by mixed carbonates and sulfates of varying composition. *F. W. Küster. Zeit. anorg. Chem.* **22**, *161* (*1899*). — Morgan (preceding review) came to the conclusion that the action of 105 carbonate as ion on barium sulfate should be counterbalanced by one sulfate as ion. This is not in accord with the facts. The discrepancy is due to hydrolysis of barium carbonate, a phenomenon overlooked by Morgan.
W. D. B.

The nature of the change from violet to green in solutions of chromium salts. *W. R. Whitney. Jour. Am. Chem. Soc.* **21**, *1075* (*1899*). — By electrolyzing a solution of green chromic sulfate in solidified Agar-Agar, the author succeeds in showing the presence of free acid in very nearly the theoretical amount. He also shows that only half the sulfate can be precipitated immediately as barium sulfate. These experiments seem to be conclusive as to the nature of the change.
W. D. B.

On the racemisation of camphor. *A. Debierne. Comptes rendus*, **128**, *1110* (*1899*). — Camphor is dissolved in toluene, aluminum chlorid added, and the solution kept at about 80° for fifteen hours. Starting with two hundred grams of camphor, the author recovered one hundred and twenty grams of a substance resembling camphor in every respect except that it was not optically active.
W. D. B.

On the mechanism of the disaggregation of hydraulic cements. *H. Le Chatelier. Comptes rendus*, **128**, *661* (*1899*). — Attention is called to the fact that if a moistened mass of cement be placed under a stress, there will be increased solubility at the point of greatest stress and the mass will be correspondingly weakened. To test this hypothesis, the author subjected a piece of dry plaster and one of moistened plaster, each to half its breaking pressure. The moistened mass broke inside of twenty-four hours, while the dry one was unchanged at the end of two months. *W. D. B.*

On the mixed halid salts of lead. *V. Thomas. Comptes rendus*, **128**, *1234*, *1329* (*1899*). — The author believes in the existence of the compounds $3PbCl_2$.

$PbBr_2$, and PbBrCl. In spite of the fact that he obtained crystals varying continuously between PbBrI and $PbBr_2$, the author takes up the cudgels in behalf of the compound $3PbBr_2.PbI_2$. *W. D. B.*

The complex oxids of the rare earths. *G. Wyrouboff and A. Verneuil. Comptes rendus*, 128, *501, 1331, 1573* (*1899*).—The authors conclude that the following oxids of cerium exist: CeO, Ce_3O_4, the peroxid, $Ce_2O_4 3CeO$, and Ce_2O_4CeO, the last of which becomes stable only when the CeO is replaced by the oxid of lanthanum, didymium, or yttrium. The authors describe a quantitative method for separating cerium from a concentrated nitrate solution by means of ammonium, sulfate, and the remaining ten percent by means of ammonium persulfate.

The authors do not believe that cerium, lanthanum, and didymium are trivalent, nor that thorium is tetravalent and they avoid some of the difficulties by assuming that the molecule of cerium oxid is polymerized to three times the formula weight and that of thorium oxid to four times the formula weight.
W. D. B.

On the synthesis of phenol from acetylene. *M. Berthelot. Comptes rendus*, 127, *908* (*1898*); *Ann. Chim. Phys.* (*7*) 17, *289* (*1899*). — Qualitative experiments on the formation of phenol when the compound of acetylene with acid potassium sulfate is heated to 200° and then acidified. *W. D. B.*

Observations on the hydrates of acetylene. *M. Berthelot. Comptes rendus*, 128, *333*; *Ann. Chim. Phys.* (*7*) 17, *297* (*1899*).—When acetylene is treated with pure sulfuric acid, the product is chiefly crotonic aldehyde; when treated with $H_2SO_4.H_2O$ the product consists of crotonic aldehyde plus some other readily oxidizable substances which have not been fully identified.
W. D. B.

Action of hydrogen on acetylene in presence of nickel. *P. Sabatier and J. B. Senderens. Comptes rendus*, 128, *1173* (*1899*). — When a mixture of hydrogen and acetylene is passed over freshly reduced nickel, there is a large quantity of ethane formed. *W. D. B.*

Studies on the phosphoric esters. *J. Cavalier. Ann. Chim. Phys.* (7) 18, *449* (*1899*)—Reviewed (3, 420, 426) from Comptes rendus, 126, 1142, 1214, 1285; 127, 60, 114 (1898).

Action of ferric chlorid and bromid on some aromatic compounds and their halid substitution products. *V. Thomas. Comptes rendus*, 128, *1576* (*1899*). — When ferric chlorid acts on *p*-dibrombenzene, the following compounds are formed: C_6Cl_5Br, $C_6H_2Cl_3Br$ (M Pt 138°), $C_6H_2Cl_3Br$ (M Pt 93°), C_6H_4ClBr (1, 4). Ferric chlorid acts on iodobenzene replacing hydrogen by chlorin. Ferric bromid acts on benzene and toluene in the same general way as ferric chlorid but less energetically. Ferric bromid acts on iodobenzene forming dibrombenzene while it attacks the chlorbenzenes with substitution of hydrogen by chlorin. (Cf. 3, 420).
W. D. B.

On a new process for preparing the silicid of iron, SiFe. *P. Lebeau. Comptes rendus*, 128, *933* (*1899*). — On fusing silicid of copper and oxid of iron

in the electric furnace, the silicid of iron thus formed dissolves in an excess of fused copper silicid. On cooling, SiFe separates in a crystalline form.
W. D. B.

On the formation of the carbide of the alkalies, of the alkaline earths, and of magnesium. *H. Moissan. Ann. Chim. Phys.* (7) 16, *145* (*1899*). — Reviewed (3, 181) from Comptes rendus, 126, 302 (1898).

Osmotic Pressure and Diffusion

Direct measurement of very dilute solutions of sodium chlorid. *A. Ponsot. Comptes rendus*, 128, *1447* (*1899*). — The author concludes from his measurements that the limiting value of the van 't Hoff coefficient *i* is 1.83 for sodium chlorid at 0° instead of two, as the dissociation theory requires.
W. D. B.

Studies in filtration. *J. Hausser. Comptes rendus*, 128, *112*, *242* (*1899*).— When using an amorphous layer such as kaolin, instead of filter paper, the rate of filtration varies inversely as the thickness of the layer. The rate is a more complicated function of the pressure under which the filtering layer is formed.
W. D. B.

Action of some gases on rubber. *d'Arsonval. Comptes rendus*, 128, *1545* (*1899*). — Carbonic acid passes very rapidly through rubber, oxygen more gradually, and nitrogen very slowly. *W. D. B.*

Velocities

On the theory of chemical reaction velocity. *S. Arrhenius. Zeit. phys. Chem.* 28, *317* (*1899*). — A further development of the author's hypothesis with regard to active and inactive cane-sugar. The interesting feature of the paper is the assumption that the addition of anything to the solution displaces the equilibrium between the two modifications. *W. D. B.*

On the decomposition of carbon monoxid in presence of the oxid of iron. *O. Boudouard. Comptes rendus*, 128, *98*, *307*, *822*, *1522* (*1899*). — At 445° the decomposition of carbon monoxid into carbon and carbon dioxid is a function of the time and of the amount of iron oxid, the reaction apparently running to an end. Nickel and cobalt oxids act in the same way but more slowly.
W. D. B.

On the explosiveness of acetylene at low temperatures. *G. Claude. Comptes rendus*, *128*, *303* (*1899*). — At −80° acetone absorbs about two thousand times its volume of acetylene under atmospheric pressure. If a platinum wire be heated red hot in this mixture by means of an electric current, nothing happens. Liquid acetylene at the same temperature does not explode in presence of a glowing wire. *W. D. B.*

On the explosive tendency of mixtures of acetylene with inert gases. *M. Berthelot and Vieille. Comptes rendus*, 128, *777*; *Ann. Chim. Phys.* (7) 17, *302* (*1899*). — The mixtures studied were chiefly acetylene and illuminating gas, the authors determining the conditions under which no explosion wave is propagated. *W. D. B.*

Electromotive Forces

Chemical proof of the concentration changes with flowing electrodes. *W. Palmaer. Zeit. phys. Chem.* 28, *257* (*1899*). — A glass stopper with a number of vertical scratches fits into a glass tube. The mercury flows through the spaces made by the scratches, thus giving the effect of over a hundred tips. With this improved flowing electrode and an apparatus designed to prevent convection currents, the author has succeeded in showing, by chemical analysis, that changes of concentration do take place at the anode and at the cathode.

W. D. B.

On flowing electrodes. *G. Meyer. Verh. phys. Ges. Berlin*, 17, *114* (*1898*); *Wied. Ann.* 67, *433* (*1899*). — A discussion of Palmaer's experiments (2, 454) in which it is shown that these prove nothing as to the relative merits of the Nernst and Warburg theories. Nernst assumes that chlorin as ion is carried down and then converted into the mercury salt; Warburg assumes the carrying down of the salt. Either view calls for a change of concentration, though not for the same change of concentration. *W. D. B.*

On the alloys of iron and nickel. *F. Osmond. Comptes rendus*, 128, *304* (*1899*). — The author has determined the temperature at which the magnetism disappears for the complete series of nickel and iron. The alloys contained small amounts of manganese and carbon. Starting from the iron end, the temperature drops from 735° to 0° as the percentage of nickel increases to 31°. The temperature next rises, reaching a maximum of 590° for seventy percent nickel and then drops off to the value of pure nickel. *W. D. B.*

The effect of low temperatures on certain steels. *F. Osmond. Comptes rendus*, 128, *1395* (*1899*). — Certain nickel steels are not magnetic at ordinary temperatures, but become magnetic at very low temperatures. The author refers this phenomenon very properly to the lowering of the transformation point by the addition of another substance. *W. D. B.*

The effect of magnetism on the heat conductivity of iron. *D. Korda. Comptes rendus*, 128, *418* (*1899*). — "The heat conductivity of soft iron decreases in the direction of the lines of magnetic force; on the other hand, it remains unchanged in the direction of the equipotential lines, regardless of the sign of the magnetic force." *W. D. B.*

Electrolysis and Electrolytic Dissociation

Electrolytic action observed near a Crookes tube. *H. Bordier and Salvador. Comptes rendus* 128, *1511* (*1899*). — Two copper electrodes dipping into copper sulfate solution were placed near a Crookes tube. After this latter had been excited for some time, it was found that there was a difference of potential between the electrodes. *W. D. B.*

Preparation of fluorin electrolytically in a copper vessel. *H. Moissan. Comptes rendus*, 128, *1543* (*1899*). — A copper U-tube can be used successfully for the preparation of fluorin, but the electrodes must still be platinum.

W. D. B.

On the Wehnelt interrupter. *d'Arsonval H. Pellat* (*2*), *A. Blondel, P. Bary, J. Carpentier, H. Amagat, E. Lagrange. Comptes rendus*, 128, *529, 732, 815, 877, 925, 987, 988, 1224* (*1899*). — A series of short notes dealing with the theory of the Wehnelt interrupter and with modifications thereof.

W. D. B.

The electrical conductivity and luminosity of flames containing vaporized salts. *A. Smithells, H. M. Dawson and H. A. Wilson. Proc. Roy. Soc.* 64, *142* (*1898*); *Zeit. phys. Chem.* 32, 303, (*1900*).—The following conclusions were drawn:

The conductivity of vaporized salt is of an electrolytic character, but there are features connected with it that distinguish it from electrolytic conduction in aqueous solution. Thus Ohm's law is only obeyed within certain limits, and the general relation between current strength and electromotive force can only be represented generally by a more complex expression.

"The conductivities of different salts differ greatly, according to the electropositive constituent.

"Among different salts of the same metal, differences of conductivity appear at the higher concentrations, but at low concentrations equivalent solutions have equal conductivity.

"The conductivity of the haloid salts as a group is distinct from that of the oxy-salts.

"The conductivity of the haloid salts of a metal among themselves increases with the increasing atomic weight of the halogen.

"The conductivity of the oxy-salts of a metal is approximately equal, and approaches that of the hydrates.

"The more easily oxidizable halogen salts are probably partly converted into oxide in the flame, so that their conductivity is composed of two parts.

"The behavior of the salts in flames supplied with chloroform vapor seems to establish the fact that the conductivity and the color produced by the salt vapor are not due to a common cause." *W. D. B.*

On the change in the resistance of metals and alloys due to torsion. *C. de Szily. Comptes rendus*, 128, *927* (*1899*). — The resistance of a wire of constantan increases with the torsion and is also a function of the time. *W. D. B.*

On the variation of the resistance of an electrolytic conductor in a magnetic field. *H. Bagard. Comptes rendus*, 128, *91* (*1899*).—An arrangement is described whereby the author has succeeded in showing that the resistance of an electrolytic conductor is affected by a magnetic field. *W. D. B.*

Dielectricity and Optics

Real polarization of dielectrics. *H. Pellat. Comptes rendus*, 128, *1218, 1312*; *Ann. Chim. Phys.* (*7*) 18, *150, 571* (*1899*).—Two of the objects of this paper are: "to show experimentally that there is a real polarization of solid dielectrics when these are submitted for a long time to the action of an electric field; and to distinguish this real polarization from the fictitious one usually assumed in order to account for the specific inductive power." In addition to the specific inductive power K, we have therefore to consider a new constant characterizing the rate at which the polarization reaches its limit, and a function of the field characterizing the limiting value of the polarization for that field.

W. D. B.

On a note by M. Pellat concerning the polarization of dielectrics. *Liénard. Comptes rendus*, 128, *1568* (*1899*). — Comment on a paper by Pellat (preceding review). *W. D. B.*

Chemical action of the electrical discharge. *M. Berthelot. Comptes rendus*, 126, *561*, *567*, *609*, *616*, *671*, *681*, *691*, *775* (*1898*); *Ann. Chim. Phys.* (*7*) 16, *5*, *21*, *31*, *41*, *55*, *67*, *81* (*1899*). — In the first paper it is shown that the silent discharge tends to dissociate organic compounds and also to promote polymerization. In the remaining six papers, it is pointed out that nearly all organic substances absorb nitrogen when a mixture of nitrogen and the organic substance is submitted to the discharge. *W. D. B.*

On the changes of rotation of active electrolytes in dilute aqueous solution. *E. Rimbach. Zeit. phys. Chem.* 28, *251* (*1899*). — The experiments confirm the conclusion that it is safe to extrapolate for infinite dilution only when this involves a slight change in the numerical value; in other words, with strong electrolytes. *W. D. B.*

On the molecular refraction, molecular dispersion, and specific rotatory power of the compounds of camphor with several aromatic aldehydes. *A. Haller and P. T. Müller. Comptes rendus*, 128, *1370*; 129, *1005* (*1899*). — From the tabulated data the authors conclude that the addition of aldehydes to camphor not only increases the molecular refraction and dispersion, but also increases the rotatory power, in some cases ten-fold. *W. D. B.*

On the rotatory power of sugar. *E. Mascart and H. Bénard. Ann. Chim. Phys.* (*7*) 17, *125* (*1899*). — An investigation undertaken primarily for technical purposes but carried out with scientific accuracy. Attention is called to the fact that, even in instruments from the best makers, the variation of the length of the tube from one decimeter may easily amount to one-half of one percent.

W. D. B.

The influence of temperature on the specific rotation of sucrose and method of correcting readings of compensating polariscopes therefor. *H. W. Wiley. Jour. Am. Chem. Soc.* 21, *568* (*1899*). — A careful study of the effect of temperature upon the rotation of sugar solutions. Attention is drawn to the fact that when using a compensating polariscope a correction must be applied for the change with the temperature of the rotation of the quartz wedge.

W. D. B.

Note on the alcohol actinometer. *C. Crova. Ann. Chim. Phys.* (*7*) 17, *22* (*1899*). — An alcohol thermometer with mercury index is used and the intensity is determined from the rise of temperature in a given time. A full description of the apparatus is given together with an account of the precautions necessary in using it. *W. D. B.*

Actinophotometer based on the relation between the brilliancy of phosphorescing zinc sulfid and the intensity or nature of the exciting light. *C. Henry.*

Comptes rendus, 128, *941* (*1899*). — The author measures the brilliancy of a zinc sulfid layer after being exposed to the light. It is claimed that this actinometer satisfies to a remarkable degree the two conditions of responding to all the radiations which reduce silver bromid, and those only, and of giving results practically corresponding to those of the photographic plate. *W. D. B.*

On the hydrogen flame. *Schlagdenhauffen and Pagel. Comptes rendus*, 128, *1170* (*1899*). — "The flame of pure or impure hydrogen becomes suddenly a violet blue when it strikes a cold substance, glass, or porcelain, under different circumstances."

"This coloration is not due to the presence of hydrogen sulfid, as claimed by Salet; but is due to hydrogen selenid." *W. D. B.*

On an intense source of monochromatic light. *C. Fabry and A. Pérot. Comptes rendus*, 128, *1150* (*1899*). — As source of light, the authors use the mercury arc in a vacuum, first studied by Arons. This consists of a violet, a green, and two yellow rays. Bichromate of potash absorbs the violet ray; a solution of didymium chlorid or of eosin absorbs the two yellow rays; sulfate of quinin absorbs the ultra violet rays. *W. D. B.*

On the source of energy in radio-active substances. *W. Crookes. Comptes rendus*, 128, *176* (*1899*). — In order to account for the apparent creation of energy out of nothing, the author assumes that the radio-active substances are so constituted that they have the property, heretofore peculiar to Maxwell's demons, of reacting with the more rapidly moving molecules, converting their energy of translation into light. This would, of course, cause a fall of temperature which might, however, be so slight as to avoid detection. By this hypothesis we save the first law of thermodynamics, but throw away the second. *W. D. B.*

On some relations between luminous and chemical energy, and on the displacement of oxygen by the halogens. *M. Berthelot. Comptes rendus*, 127, *795* (*1898*); *Ann. Chim. Phys.* (*7*) 17, *320* (*1899*). — Iodin does not react with oxygen nor decompose water either in the dark or in the light. Bromin decomposes water perceptibly in the sunlight, practically not at all in the dark. *W. D. B.*

Chemical action of X-rays. *P. Villard. Comptes rendus*, 128, *237* (*1899*). — If a photographic plate be exposed to X-rays and then to sunlight, the latter effect apparently reverses the former. The author has made an ingenious application of this. He takes an X-ray photograph and then exposes the plate to light. The sunlight has a positive effect on the portions which have been sheltered from the X-rays and neutralizes the effect of the X-rays more or less completely over the rest of the plate. It is thus possible to prepare a positive instead of a negative. *W. D. B.*

A PRELIMINARY INVESTIGATION OF THE CONDITIONS WHICH DETERMINE THE STABILITY OF IRREVERSIBLE HYDROSOLS[1]

BY W. B. HARDY

It has long been held that a large number of colloidal solutions are related to or identical with suspensions of solid matter in a fluid in which the particles of solid are so small as to settle at an infinitely slow rate. Such solutions are the colloidal solutions of metals and of sulphides, such as those of antimony, arsenic, and cadmium. Such solutions belong to the class of irreversible colloidal mixtures. A rise of temperature assists the process of coagulation or precipitation;[2] but neither a further rise nor a fall of temperature will cause the reformation of the hydrosol. On this ground they may provisionally be classed with such colloidal solutions as those of silica, ferric hydrate, alumina, etc., and with the modification of the albumen of white of egg which is produced by heating an aqueous solution to the boiling-point. I also add to the class, for reasons to be developed in the following pages, the suspension of mastic in water which is produced by adding a dilute alcoholic solution of the gum to water.

Looked at from the point of view of the phase rule, the equilibrium in these hydrosols, if they really consist of minute solid particles dispersed in a fluid, is not necessarily between the solid particle and water, but between the solid particle and a solution of the particular solid in water. The hydrosol of gum mastic gives off a vapor of the gum of a density sufficient to

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[1] Read before the Royal Society, January 25, 1900.

[2] Elsewhere (Journal of Physiology, 24, 172 (1899), I have shown that precipitation and coagulation are not discontinuous processes. Coagulation gives way to precipitation when the concentration of the solid phase falls below a certain amount.

affect the olfactory organs, and, therefore, the water must contain a definite quantity in solution. Similarly, as it is probable that no substance is completely insoluble, we may assume that in all the examples a portion of the solid is in true solution in the fluid. As the solid which is not in true solution is dispersed in particles whose diameter is, as a rule, very much smaller than the mean wave-length of light, it follows that the surface of contact between solid and fluid is very great for unit mass of the former. The opportunity for evaporation and condensation of the solid matter of the particles afforded by the immense surface of contact is so very great that, although only an immeasurably minute quantity of the solid may be in true solution at any one time, this quantity, minute though it be, is probably an important factor in determining the equilibrium between solid and fluid.

It is necessary to keep such considerations as this in mind in view of the readiness with which these mixtures have been regarded as simple suspensions[1] in which the only relation between solid and fluid is a mechanical one. These hydrosols are, as a matter of fact, singularly stable when pure. They can, for instance, be concentrated by boiling to a remarkable extent, and their stability depends upon complex relations between fluid and solid, which give the former, so to speak, a definite hold over the latter.

Mode of preparation of the different solutions. — The hydrosol of gold was prepared by adding a couple of drops of a solution of phosphorus in ether to about a litre of a very dilute solution of gold chloride. The fine ruby-coloured fluid which was formed was dialysed against distilled water[2] for fourteen days, and then concentrated by boiling. The hydrosol of silicic acid was prepared by acting on soluble glass with excess of hydrochloric acid, and dialysing the product. A hydrosol of ferric

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[1] Cf., for instance, Stoeckl and Vanino. Zeit. phys. Chem. 30,98 (1899); also Ostwald, 'Lehrbuch.'

[2] In working with these colloidal solutions it is very necessary to use distilled water freed from dissolved carbonic acid.

hydrate was prepared by prolonged dialysis of the solution in ferric chloride.

The hydrosol of gum mastic was prepared by adding a very dilute solution of the gum in alcohol to distilled water. It was dialysed for fourteen days against distilled water. The hydrosol of heat-modified egg-white was prepared by dissolving white of egg in nine times its volume of distilled water, filtering and boiling. The result should be a brilliant fluid which scatters blue light. Surface action, however, plays an extraordinary part. If the solution is boiled in a test-tube a milky fluid is formed and a film of proteid is left on the glass; a second quantity boiled in the same test-tube comes out less milky, until, when the proteid film is sufficiently thick to eliminate all action by the glass, the solution after boiling contains the proteid dispersed as particles so small that they scatter pure blue light. After preparation the hydrosol was dialysed against distilled water for some days.

Behaviour of the Hydrosols in an Electric Field.—It has long been known that the particles in these colloidal solutions move in an electric field. Zsigmondy[1] found that the gold in colloidal solutions moves against the current. Picton and Linder[2] established the important fact that the direction of movement of the particles, as compared with the direction of the current, depends upon their chemical nature. I have shown that the heat-modified proteid is remarkable in that its direction of movement is determined by the reaction, acid or alkaline, of the fluid in which it is suspended.[3] An immeasurably minute amount of free alkali causes the proteid particles to move against the stream, while in the presence of an equally minute amount of free acid the particles move with the stream. In the one case, therefore, the particles are electro-negative in the other they are electro-positive.

Since one can take a hydrosol in which the particles are electro-negative and, by the addition of free acid, decrease their

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[1] Liebig's Ann. 301, 29 (1898).

[2] Jour. Chem. Soc. 70, 568 (1897).

[3] "The Coagulation of Proteid by Electricity," W. B. Hardy. Journal of Physiology, 24, 288 (1899).

negativity, and ultimately make them electro-positive, it is clear that there exists some point at which the particles and the fluid in which they are immersed are iso-electric.

This iso-electric point is found to be one of great importance. As it is neared, the stability of the hydrosol diminishes until, at the iso-electric point, it vanishes, and coagulation or precipitation occurs, the one or the other according to whether the concentration of the proteid is high or low, and whether the iso-electric point is reached slowly or quickly, and without or with mechanical agitation.

This conclusion can be verified experimentally in many ways. If a coagulum or precipitate of the proteid particles made either by the addition of a neutral salt, or by the addition of acid or alkalies, be thoroughly washed, made into a fine mud in an agate mortar, and suspended in water in a U-tube, it rapidly subsides. The establishment of an electric field having a potential gradient of 100 volts in 10 cm has no influence on the level of water or precipitate in forty-eight hours. If, now, the smallest possible amount of caustic soda or acetic acid be added, the proteid will commence to move, so that in twenty hours the precipitate will rise in one or other limb until it nearly touches the platinum electrode.

Speaking generally, the hydrosol of ferric hydrate is stable only in the absence of free acids or alkalis or neutral salts. The hydrosol of heat-modified proteid is stable only in presence of free acid or alkali. The hydrosol of gum mastic is readily precipitated by acids, but is stable in presence of any concentration of monovalent alkalis. The general conditions of stability of these various hydrosols, therefore, are very different, yet they agree in manifesting the same important relation between the iso-electric point and the point of precipitation as is shown by the hydrosol of proteid.

In the hydrosol of ferric hydrate the particles are markedly electro-positive. A dilute hydrosol is coagulated by citric acid when the concentration of the latter reaches 1 gram-molecule in 4,000,000 cc. No matter how small the concentration of the ferric hydrate, the hydrosol becomes cloudy and settles. The rate of settling is, however, slow, being about 1 cm an hour. In an electric field, having the form of a U-tube, the particles always settle slightly faster from the negative electrode — the acceleration due to the electric field being about 5 mm an hour. The suspended particles of ferric hydrate show, therefore, an exceedingly slight movement in a direction *opposite* to that which they manifest when in colloidal solution. In the latter condition they are markedly electro-positive; in the former they are exceedingly faintly electro-negative. An exceedingly faint electro-negative character is also conferred upon the ferric hydrate when the hydrosol is coagulated by ammonia, 1 gram-molecule of the latter being present in 100,000 cc.

If a fresh gel of silica is broken up in distilled water and carefully washed to free it from still uncoagulated silica, and from impurities, it is completely iso-electric with the water. It becomes markedly electro-negative, however, on the addition of the minutest trace of free alkali.

Gum mastic precipitated from a dilute hydrosol by adding barium chloride until the concentration is 1 gram-molecule in 600,000 cc is found to be iso-electric with the fluid. It is markedly electro-negative when in colloidal solution.

Picton and Linder have shown that the particles in these hydrosols gradually grow in size as the coagulation or precipitation point is neared.[1] It might, therefore, be urged that, as the movement of the particles in the electric field is, on Quincke's theory of electric endosmose, due to surface action the fact that they do not move when in simple suspension as opposed to colloidal solution may be due to the diminution of the impelling force acting on a given volume.[2] This is, however, negatived by the character of the experiments. The addition of a minute amount of free alkali to a mass of particles of coagulated silica

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[1] Jour. Chem. Soc. 61, 148 (1892).

[2] As a matter of fact, Lamb finds that the velocity of a particle is independent of its size or shape, provided that its dimensions are large compared with the slip, so perhaps the objection scarcely needs discussion. Lamb, Brit. Assoc. Report, 1887, p. 502.

which have settled to form a "mud" cannot alter the size of these relatively very large masses to any appreciable extent. And since in the case of ferric hydrate and proteid, the sign of the charge which the particles carry in the electric field is different on each side of the actual point of precipitation, that point must of necessity be an iso-electric point.

If the stability of the hydrosol is dependent upon a difference in electrical potential between the solid particles and the fluid, then one would expect that, for at any rate a short distance from the iso-electric point, the stability would vary simultaneously with the variation in the difference of potential. The experimental investigation of this question is beset by many difficulties. At present I know of no way of approaching the iso-electric point other than by the addition of salts, acids, or alkalis. One may, therefore, approach the point by the addition of, say, acid or alkali, and use a salt to measure the stability of the system, as in the experiment described later. In such experiments, however, the colloid particles are immersed in a complicated system of three components, the conditions of equilibrium of which cannot be arrived at from existing data. The conditions could be simplified by using, say, KHO or H_2SO_4 to approach the iso-electric point, and K_2SO_4 as the measure of the change of stability. A series of determinations with different systems of this kind may afford the requisite measurements.

A direct and conclusive proof that stability does decrease as the iso-electric point is approached was however obtained in two ways. The iso-electric point can be approached in the case of the hydrosol of proteid by the withdrawal of either the free acid or the free alkali, as the case may be. As it is neared, the proteid particles increase in size, so that instead of scattering blue light, they scatter white light; thus the surface of contact of fluid and solid gradually diminishes as the point is neared. The second experiment, though not a quantitative one, is very convincing. A hydrosol of gum mastic dialysed as pure as possible is not destroyed by mechanical agitation even when long continued. If, however, a salt is added in an amount so small that it just fails to coagulate the hydrosol, the latter is rendered so unstable that it is destroyed by shaking.

Experiments were made to determine whether the particles actually carry a charge. An electric field which was practically uniform was made by using flat electrodes of the same size, which were placed parallel to one another at the ends of a straight tube. The particles were found to move in all parts of the field; they therefore carry a definite charge which, according to Quincke's theory of the movement of particles in an electric field, would be a surface charge, each particle being surrounded by a double layer of electricity.

Action of salts. — The power possessed by salts of destroying colloidal solutions was noticed by Graham. The subject was, however, first accurately investigated by H. Schulze.[1] He showed that the power which various salts possess in precipitating a hydrosol of sulphide of arsenic is related to the valency of the metal, while the valency of the acid has little influence. The increase in the precipitating or coagulating power produced by increase in valency is very great. If coagulative power be defined as the inverse of the concentration in gram-molecules per litre necessary to convert a given hydrosol into a hydrogel, then from Schulze's measurements the coagulative power of metals of different valency is:

$$R' : R'' : R''' = 1 : 30 : 1650.$$

Schulze's conclusions were verified by Prost,[2] who used sulphide of cadmium, and Picton and Linder, who used the sulphide of antimony.[3] The last-named workers added the important fact that a small portion of the coagulating salt is decomposed, the metal being entangled in the coagulum.

The measurements which I have made with various colloidal solutions both confirm Schulze's results, and bring out a new relation which may be stated as follows:

The coagulative power of a salt is determined by the valency

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[1] Jour. prakt. Chem. 25, 431 (1882).

[2] Bull. Acad. roy. Belg. (3) 14, 312 (1887).

[3] Jour. Chem. Soc. 67, 63 (1895).

of one of its ions. This prepotent ion is either the negative or the positive ion according to whether the colloidal particles move down or up the potential gradient. The coagulating ion is always of the opposite electrical sign to the particle.

The salts employed to determine this point were the sulphates of aluminium, copper, magnesium, potassium, and sodium; the chlorides of copper, barium, calcium and sodium, and the nitrate of cadmium. Solutions containing 1 gram-molecule in 2000 cc were prepared.

The experiments may be summarised as follows:

Silica, dialysed free from chlorides, electro-negative
Concentration of coagulating salt 1 gram-mol in 120,000 cc
Temperature 16°

Coagulated at once	In 10 minutes	In 2 hours	In 24 hours	Still fluid
$Al_2(SO_4)_3$	$CuSO_4$ $CuCl_2$ $Cd(NO_3)_2$ $BaCl_2$	$MgSO_4$	K_2SO_4 Na_2SO_4	NaCl Control

This illustrates many experiments.

Proteid in presence of a trace of alkali, electro-negative
Temperature 16°. Coagulating salt 1 gram-mol in 80,000 cc

Coagulated at once	On slightly warming	Did not coagulate
$Al_2(SO_4)_3$ $Cd(NO_3)_2$ $CuSO_4$ $CuCl_2$	$MgSO_4$ $BaCl_2$ $CaCl_2$	Na_2SO_4 K_2SO_4 NaCl

Proteid in presence of a trace of acetic acid, electro-positive

Coagulated instantly	No coagulation
$Al_2(SO_4)_3$ $CuSO_4$ K_2SO_4 Na_2SO_4 $MgSO_4$	$CuCl_2$ $Cd(NO_3)_2$ $BaCl_2$ NaCl

Mastic, dialysed, neutral, electro-negative
Temperature 16°. Concentration of coagulating salt, 1 gram-mol in 50,000 cc

Coagulates at once	No coagulation
$Al_2(SO_4)_3$	K_2SO_4
$CuSO_4$	Na_2SO_4
$CuCl_2$	$NaCl$
$Cd(NO_3)_2$	
$MgSO_4$	
$BaCl_2$	

Ferric hydrate, dialysed, neutral, electro-positive
Temperature 16°. Coagulating salt 1 gram-mol in 100,000 cc

Coagulates at once	Does not coagulate
$Al_2(SO_4)_3$	$CuCl_2$
$CuSO_4$	$Cd(NO_3)_2$
$MgSO_4$	$NaCl$
K_2SO_4	$BaCl_2$
Na_2SO_4	

Gold, dialysed for fourteen days against distilled water, very faintly acid. Electro-negative
Temperature 16°. Coagulating salt 1 gram-mol in 200,000

Red changes to blue[1] instantly	No change
$Al_2(SO_4)_3$	$NaCl$
$CuSO_4$	Na_2SO_4
$CuCl_2$	K_2SO_4
$Cd(NO_3)_2$	
$MgSO_4$	
$BaCl_2$	

Only one comment on these experiments is needed. Solutions of $Al_2(SO_4)_3$, $Cd(NO_3)_2$, $CuCl_2$, and $CuSO_4$, are acid to lit-

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[1] The relation of the colours of hydrosols of gold to the size of the particles has been investigated by Stoeckl and Vanino. Zeit. phys. Chem. 30, 98 (1899). The change from red to blue indicates an increase in the size of the particles.

mus, while $MgSO_4$, and $BaCl_2$ are neutral to litmus, but acid to phenol phthalein. This acidity has a disturbing action in some cases — the system acts not only as a neutral salt, but also as a free acid. Thus the hydrosol of proteid when brought very near to the point of precipitation by dialysis is more sensitive to the more acid than to the less acid salts of the bivalent metals. The effect of the acid or basic reaction of the salt on the hydrosol is as a rule small compared with the effect of the metal ion. Thus the stability of a hydrosol of electro-positive proteid is increased by free acid, yet the acid salts find their proper place in the scale of valency. Again, ferric hydrate is coagulated by nitric acid when the concentration reaches 1 gram-mol in 2,500 cc; yet the cadmium salt of this acid is not much more potent than the "neutral" salts $MgSO_4$, $BaCl_2$.

Temperature 16°. Concentration necessary to coagulate ferric hydrate

Salt	cc
K_2SO_4	1 gram-mol in 4,000,000
$MgSO_4$	" " 4,000,000
$BaCl_2$	" " 10,000
NaCl	" " 30,000
$Cd(NO_3)_2$	" " 50,000

The extraordinary rise in coagulative power with an increase in valency, which was observed by Schulze, Prost, and Picton and Linder, holds in all cases. In order to measure it for ferric hydrate, I used Schulze's method in which a drop of the hydrosol is allowed to fall into a large volume of the solution of the salt. A number of experiments were made until the concentration of the salt was found which just sufficed to coagulate the drop. In the case of gold and mastic the process was reversed, the salt solution being added drop by drop to a measured quantity of the hydrosol. I append the results:—

Gum mastic, neutral. Temperature 40°

Salt	cc
$BaCl_2$	1 gram-mol in 86,000
NaCl	" " 8,000
$MgSO_4$	" " 68,000
K_2SO_4	" " 8,000

Gold, very faintly acid. Temperature 16°

Salt	cc
NaCl	1 gram-mol in 72,000
$BaCl_2$	" " 500,000
K_2SO_4	" " 75,000

The figures for ferric hydrate have already been given. It has been pointed out that if specific molecular coagulative power be defined as the inverse of the volume occupied by one gram-molecule of a substance when it just suffices to bring about coagulation, then this value (K) varies with the valency of the active ion approximately according to the square and cube:—

$$R' : R'' : R''' = K : K^2 : K^3.$$

The relation really is not as simple as this; it is complicated by the change which the specific molecular conductivity of a salt undergoes with change in concentration. The theoretical considerations have been dealt with elsewhere.[1] For convenience of description, however, I will call this relation the relation of the square and cube.

Action of acids and alkalis.—The values for K furnished by these substances show relations to valency even more interesting than that found with salts. As in the case of salts, their action is entirely dependent upon the electric properties of the colloid particles.

When the colloid particles are electro-negative alkalis either do not cause precipitation at any concentration, or if they do cause precipitation the value of K does not vary in any simple way with variations in valency.

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[1] Hardy and Whetham, Journal of Physiology, 24, 288 (1899) and Whetham, Phil. Mag., November, 1899.

When the particles are electro-positive, K increases with valency but the relation of the square and cube does not hold. Instead, one finds that K varies directly with the chemical activity of the solution.

Acids have the reverse relations. When the particles are electro-negative, the value of K varies directly with the chemical activity of the solution; while if these particles are electro-positive, acids either have no precipitating power, or if K has any value, then (in the particular case measured) the value varies with valency according to the square and cube.

The various measurements are brought together in the following table. The specific conductivities were calculated from the British Association tables.[1]

COAGULATING SOLUTION

Hydrosol		Concentration necessary to produce coagulation		Specific conductivity of coagulating solution at 18° $\times 10^{12}$	Temperature
		1 gram-mol in cc =	Gram equiv per liter		
Mastic, electro-negative	Ammonia	0	∞	..	16–100°
	NaOH	0	∞	..	16–100
	KOH	0	∞	..	16–100
	$Ba(OH)_2$	40,800	0.048	100	16
	H_3PO_4	194,400	0.015	13.9	17
	Acetic acid	1,360	0.7	12.6	17
	HCl	260,000	0.004	14.5	17
	HNO_3	260,000	0.004	14.3	17
	H_2SO_4	460,000	0.004	13.2	17
	Oxalic acid	220,000	0.009	14.4	17
	$BaCl_2$	86,000	0.022	[20]	40 [2]
	$MgSO_4$	68,000	0.028	[18]	40
	NaCl	8,000	0.12	[110]	40
	K_2SO_4	8,000	0.24	[250]	40
Gold, electro-negative	Ammonia	0	∞	..	17–100
	NaOH	11,800	0.08	152	17
	KOH	10,800	0.09	189	17
	$Ba(OH)_2$[3]	12,000	0.16	..	100

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[1] "The Electro-chemical Properties of Aqueous Solutions." T. C. Fitzpatrick, 'Brit. Assoc. Report,' 1893.

[2] The values for specific conductivity are given for a temperature different from that of observation, but they serve to show the general relation.

[3] Solution saturated at 17° has no action.

COAGULATING SOLUTION — (*Continued*)

Hydrosol		Concentration necessary to produce coagulation		Specific conductivity of coagulating solution at 18° × 10^{13}	Temperature
		1 gram-mol in cc =	Gram equiv per liter		
Ferric hydrate, electro-positive	$Ca(OH)_2$[1]	..	..	..	17°
	HCl	123,000	0.008	29	17
	H_2SO_4	238,544	0.0084	26	17
	NaCl	72,000	0.013	13	17
	$BaCl_2$	500,000	0.004	4.4	17
	K_2SO_4	75,000	0.026	28	17
	KOH	1,000,000	0.001	2.2	16
	$Ba(OH)_2$	2,000,000	0.001	2.3	16
	HCl	1,800	0.5	1650	16
	HNO_3	2,000	0.5	1589	16
	H_2SO_4	1,000,000	0.002	6.8	16
	Oxalic acid	1,000,000	0.002	3.4	16
	Citric acid[2]	4,000,000	0.0007	[0.7]	16
	K_2SO_4	3,200,000	0.0006	0.77	16
	$MgSO_4$	4,000,000	0.0005	0.5	16
	$BaCl_2$	6,000	0.3	255	16
	NaCl	20,000	0.5	28	16

The figures in the fourth column are very remarkable. When the particles are electro-negative, equicoagulative solutions of acids agree in their electric conductivity within the limits of experimental error. The same relation is clearly shown if one takes the measurements which Picton and Linder made of the power possessed by acids of coagulating the hydrosol of arsenious sulphide.

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[1] No action when saturated.

[2] Specific conductivity by analogy with similar acids will not be greater than the value given.

Acid	Value of K referred to Al_2Cl_6 as unity	Sp mol conductivity when 1 gram equiv = 1000 cc
HBr	0.001	2950
HI		
HCl		
HNO_3		
H_2SO_4	0.0006	1935
Oxalic	0.0005	578
H_3PO_4	0.00007	230

When, however, the particles are electro-positive, the conductivity of equicoagulative strengths of acids varies to a remarkable extent.

Acids	H′	H″	H‴
Mastic, electro-negative	12.6	14.4	13.9
Ferric hydrate, electro-positive	1650	6.8	0.7

Now specific conductivity (C) has the relation

$$C = na(u + v)$$

where a is the fraction of the total number of molecules (n) which are dissociated at any one moment, and $u + v$ is the sum of the velocities of the two ions. The factor $u + v$ plays an important part as will be seen by comparing the values for na in equicoagulative solutions of acids with slowly moving ions with those with rapidly moving ions:—

	na
H_3PO_4	0.01
Acetic acid	0.07
HCl	0.004
H_2SO_4	
HNO_3	

This, however, is probably partly due to the fact that owing to the manner in which the coagulative power was measured, time has practically a constant small value. The values for n might, perhaps, be different if the duration of the experiments were prolonged indefinitely.

The important point, however, which calls for notice is that the function $a(u + v)$ is a numerical measure of the chemical activity of the substance at a given concentration, so that we reach the important conclusion that *the concentration of acids necessary to coagulate electro-negative colloid particles, and of alkalis necessary to coagulate electro-positive particles is determined by the laws which govern ordinary chemical equilibrium.*

In the case of the action of salts on these hydrosols, the relation is not so simple. K does not vary directly with $a(u + v)$, but contains a factor which is approximately squared or cubed by a change from a mono-valent to di- or tri-valent ions. The relation can therefore be best expressed as

$$K = na(u + v)A^x$$

where x is positive and increases rapidly with an increase in the valency of the ion whose electric charge is of the opposite sign to that on the particles.

I should interpret these relations by the suggestion that in the former the acid or alkali alters the difference of potential at the surface of the particles by altering the character of the fluid, and in that way modifies the stability of the hydrosol; in the latter the active ions of the salt act directly upon the solid particles, or, perhaps, on the charge which these carry, and thus play a part which is, perhaps, generally similar to the action of ions when they furnish nuclei for the condensation of vapor. Picton and Linder have shown that the active ions are actually entangled in, and form part of the coagulum.[1]

The former relation may profitably be placed beside Brühl's conclusions that the action exerted by a fluid upon the substance dissolved in it is determined by the chemical characters of the former, as well as of the latter. He has shown that the molecular refraction, the dielectric coefficient, and the power possessed

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[1] Jour. Chem. Soc. 67, 63 (1895).

by the fluid of dissociating or chemically changing the molecules of the substance dissolved in it are measured by the unsatisfied valency, or, to use another phrase, the residual energy of its molecules.

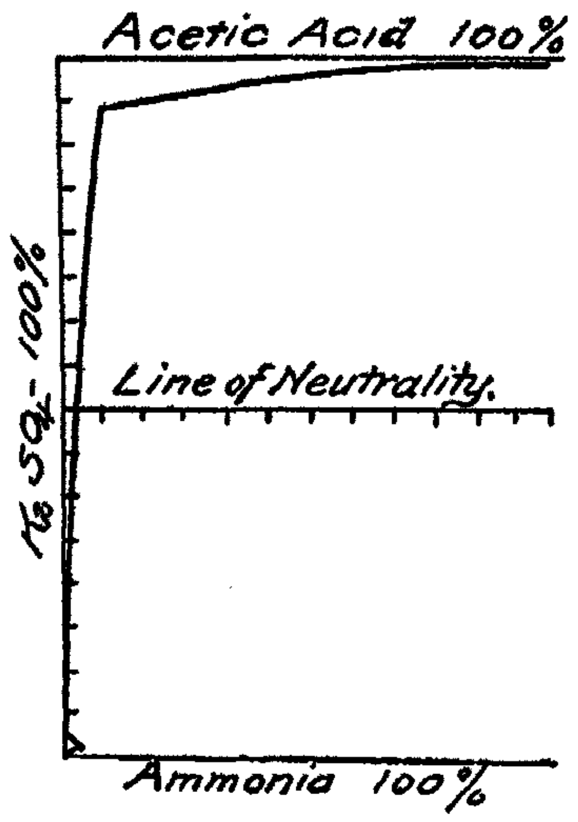
The action of acids or alkalis on a hydrosol, the particles of which are of the opposite electrical sign, seems to be compounded of these two actions. The acid or alkali may act as a salt, and exhibit the characteristic relation between K and the valency of the ion of the opposite electrical sign. An instance is furnished by the action of various acids on ferric hydrate. Or the acid or alkali by *increasing* the difference of potential between the fluid and the solid particles may increase the stability of the hydrosol. This is markedly manifested by the increased stability given to the hydrosol of gum mastic by the addition of univalent alkalis. In the action of barium hydrate on this hydrosol, the segregating action of the metal ion overcomes the action exerted by the reagent in virtue of its alkalinity, the result is that the coagulative concentration of the alkali $Ba(OH)_2$ gives a value for K which is less than that given by salts of bivalent metals, and the specific conductivity of the solution is of the same order as that of the coagulating concentration of salts of univalent metals. Against these suggestions, however, must be set the anomalous relations of the various alkalis to the hydrosol of gold.

Action of a salt in presence of varying amounts of acid or alkali

This was measured for one salt only, potassium sulphate, the colloidal solution being gold. The figures are as follows:—

Temperature 16°

	Concentration 1 gram-mol. in—cc	Concentration of the salt necessary to produce blue tint. 1 gram-mol. K_2SO_4 in—cc
Acetic acid	1,087	0
	16,000	324,000
	66,000	64,000
	330,000	50,000
	(neutral[1])	28,500
Ammonia	113,333	10,000
	22,666	9,000
	4,900	20,000
	2,450	24,000
	980	20,000
	200	Large amount of salt needed.
	100	Salt unable to act when saturated at 16° or at 100°.



Action of potassium sulphate in presence of varying amounts of acetic acid or ammonia upon the hydrosol of gold. The abscissæ represent the volume of water which holds 1 gram-molecule of the salt. The positive ordinates represent the reciprocals of the volume which holds 1 gram-molecule of the acid, and the negative ordinates the reciprocals of the volume which holds 1 gram-molecule of the alkali. Each division = 50,000 cc.

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[1] Except for a faint acid reaction of the gold solution due probably to a trace of phosphoric acid.

These results are shown in the curve. Ammonia alone will not aggregate the particles of gold. Up to a certain point, however, it decreases the stability of the system.

The conclusions can be summarised as follows:—The irreversible hydrosols which have been investigated are systems composed of solid particles dispersed through a solution of the substance of the solids in the water.

The stability of the system is related to the contact difference of potential which exists between the solid and the fluid phases, and which forms round each solid particle a double electric layer. Such double electric layers round particles of any kind immersed in a fluid would resist any movement of the particles through the fluid, because, as Dorn's experiments show, electric work is done in displacing the particles.[1] The effect would be the same as if the viscosity of the fluid was increased.[2]

The stability of the system may be destroyed by altering the difference of potential. Free acid, added to a hydrosol in which the particles are negative to pure water, will diminish the relative difference of potential of the water. In this case the reagent acts directly on the water, and the coagulative activity of unit mass of the substance varies directly with its chemical activity when dissolved in water. The same relation seems to hold when free alkali is added to a hydrosol in which the particles are electro-positive.

The stability of the system may also be destroyed by induction, the active agents being free ions carrying a static charge.[3] In this case the action may be said to be on the particles, or rather on the electric layers immediately around them, and the active ions are those whose electric sign is the opposite of that of the charge on the surface of the particles. In this case coagulative power does not vary directly with variations in chemical activity. It rises exceedingly rapidly with a rise in the valency of the active ion so that the relation

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[1] Wied. Ann. 10, 70 (1880).

[2] This mode of stating the result I owe to Prof. J. J. Thomson, and I gladly acknowledge his kindness in discussing this and kindred points with me.

[3] Whetham. loc. cit.

$$I' : I'' : I''' = n : n^2 : n^3$$

is approximately satisfied.

Picton and Linder have shown that when the concentration of the salt is insufficient to completely destroy the system, it is not wholly without action. A fresh point of equilibrium between solid and fluid is reached by an increase in the size of the particles and therefore a diminution in the extent and curvature of the surface of contact. The fact is of importance, because it introduces us to the possibility that the reagent may affect the size of the particles by altering the equilibrium between the part of the solid in solution and the part in suspension. Double electric layers around each particle are, according to Thomson, separated by a region of "uncompleted chemical combination" between the components.[1] The density of the field round the particles in hydrosols will therefore be a measure of the velocity of the solution and condensation between the particle and the liquid, and therefore the factor which determines whether the particles will on the whole grow, diminish, or remain stationary in size.

When acids or alkalies are added to hydrosols holding particles of the opposite electric sign to themselves, the simplest relation seems to be that univalent acids or alkalis increase the stability ; bivalent acids or alkalies decrease it.

The view advanced in this paper implies that each particle in a hydrosol is surrounded by a zone in which the components are in a condition of chemical instability. According to Rayleigh,[2] such a zone is of finite thickness, and deep enough to contain several molecules. We therefore have in these hydrosols two phases, separated by a layer of extraordinarily large extent, which possess considerable chemical energy. This, it seems to me, suggests an explanation of the catalytic power so markedly manifested by hydrosols.

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[1] Discharge of Electricity through Gases. Scribner, 1898, p. 24.

[2] Thomson. loc. cit. p. 26; Rayleigh. Phil. Mag. 33, 468 (1892).

ON THE MECHANISM OF GELATION IN REVERSIBLE COLLOIDAL SYSTEMS[1]

BY W. B. HARDY

Speaking generally, colloidal matter occurs in three conditions:

(1) As fluid mixture, colloidal solutions, or sols, as Graham called them;

(2) Solid mixtures of fluid and solid, the gels; and

(3) Solids, such as dry silica or dry glass.

The property of forming gels is not possessed by all those mixtures which have been classed as colloids. Some only form slimes, which even to the point of actual drying retain the fluid property of flowing. Serum albumen and water is an instance.

Those which form gels fall into two well-defined classes, according to whether the change from the sol to the gel is, or is not, reversible by a reversal of the conditions which produce it. Silica and water may be taken as the type of the latter, gelatine and water of the former. When a hydrosol of silica forms a hydrogel, the latter is "insoluble." To this class belong hydrosols of metallic hydrosulphides and oxides. A hydrosol of gelatine sets to a hydrogel by lowering the temperature; the process is however reversed when the temperature is again raised. As the inner mechanism of the gelation of the hydrosols must differ in the two cases, since in the one irreversible, in the other reversible molecular aggregates are formed, I propose to distinguish the processes by different names. The production of an insoluble gel I will call "coagulation," of a soluble gel "setting." This nomenclature is in accordance with general usage.

Temperature is the most potent factor in determining whether a mixture which forms a reversible gel is in the sol or

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[1] Read before the Royal Society, January 25, 1900.

gel state. There is also a limiting concentration of the solid below which the gel state is impossible at any temperature.

"Setting," as a rule, follows on a fall of temperature. Caseine, the chief proteid of milk, furnishes, I believe, the only known exception. In the presence of a small quantity of free alkali it forms a hydrosol. When a small quantity of a solution of calcium chloride or nitrate is added to this, a mixture is produced which forms a hydrogel on warming, and which reforms the hydrosol on again cooling.[1]

Part I. Reversible colloids

Systems containing two or three components occur, that is, binary or ternary mixtures. The binary system, agar-and-water, was studied at considerable length; and initial experiments were made with the ternary systems, gelatine-water-alcohol, gelatine-water-mercuric chloride, and agar-water-alcohol. These mixtures are homogeneous when heated, but, on cooling, there occurs a division into two fluid phases. In the binary systems and in the ternary system agar-water-alcohol, the conjugate phases have approximately the same refractive index. In the ternary system, gelatine-water-alcohol, the refractive index of the one phase differs so much from that of the other as to permit of direct microscopical investigation of the form of the surface which separates the phases. For this reason I propose to treat this ternary system first.

The ternary system — gelatine-water-alcohol

When 13.5 grams of dry gelatine are dissolved in 100 cc of a mixture of equal volumes of absolute alcohol and water, a system is produced which is clear and homogeneous at temperatures above 20°. As the temperature falls below this limit a clouding occurs, which I find to be due to the appearance of fluid droplets which gradually increase in size until they measure 3μ. On cooling further these fluid droplets become solid, and they begin to adhere to one another. In this way a framework is built up, composed of spherical masses hanging together in linear rows

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[1] Sidney Ringer. Journal of Physiology, 11, 464 (1890).

which anastomose with one another. The framework therefore, is an open structure, which holds the fluid phase in its interstices. The macroscopical result of the change is the conversion, with falling temperature, of the fluid into a loose gel. The droplets can be readily separated from the interstitial fluid by the help of a centrifugal machine.

The phenomena above described undoubtedly depend upon the separation of a homogeneous mixture into two phases owing to a fall of temperature. Each phase contains water, alcohol, and gelatine, and the system may be described as a conjugate composed of a fluid solution of gelatine in a mixture of water and alcohol, and a solid solution of water with a trace of alcohol in gelatine. Both phases, however, are fluid within a small range of temperature. The surface of separation of the two phases is curved, and at first discontinuous, and owing to the small size of the droplets it is very large.

When the gel is heated the two phases again mix to form a clear fluid. Owing however to the fact that the droplets adhere to one another, they tend to fuse as temperature rises, so as to form irregular masses of viscous fluid, which are separated from the other phase by a surface of no particular shape. The irregular form of this surface, and the ease with which it is modified by any chance slight currents, show that at this stage the surface-tension between the two phases must be exceedingly slight. In order to simplify the description, I shall call that phase which separates as small spheres the "*internal phase.*"

The concentration of the gelatine in the mixture exerts a very remarkable influence upon the configuration of the hydrogel. When it is present in large quantity the internal phase is less viscous and of smaller gelatine content than the external phase, and on cooling it is the external phase which becomes a solid solution. The effect of increasing the proportion of gelatine above a certain amount is therefore very striking — it, so to speak, turns the system inside out, so that the gel is composed of a continuous framework of solid solution, out of which are hollowed spherical spaces filled with fluid. The general mechanical properties of the gel, built on this plan, naturally differ very much from those of a gel with a small proportion of gelatine, which consists of an open framework of solid holding fluid in its interstices.

A mixture of gelatine, water, and alcohol is a ternary mixture which resembles a mixture of benzene, acetic acid, and water. In each there are two immiscible substances and a common solvent. The immiscible substances are gelatine and alcohol in the one case, and benzene and water in the other, while the common solvent is water in the former and acetic acid in the latter case. In both systems the solubility of the immiscible substances in the common solvent varies widely. Thus acetic acid and water, and water and alcohol, mix readily with rise of temperature; while acetic acid and benzene, and water and gelatine mix freely only when the temperature is above 15° in the former case, and above 40° in the latter case. Duclaux's researches[1] show that in ternary mixtures having this last characteristic the distribution of the constituents in the two phases varies widely with variations in the composition of the whole mass.

These different characters are illustrated by the following figures, which give the amount of gelatine present in grams per 100 cc. They are, however, only approximate for the solid phase, owing to the difficulty in separating it completely from the fluid phase.

Temperature 15°

Total mixture	Internal phase	External phase
6.7	17.0	2.0
13.5	18.0	5.5
36.5	8.5	40.0

The temperature at which the internal and external phases in this ternary system mix was found to be altered by altering the ratio of the masses of the components. Increasing the proportion of either of the two immiscible components, alcohol or

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[1] Ann. Chim. Phys. (5) 7, 264 (1876).

gelatine, was found to raise the temperature, while an increase in the proportion of the common solvent water was found to lower it.

The curvature of the surface which separates the phases was found not to be constant for a given mixture. The internal phase formed droplets which were large or small according to whether the mixture was cooled slowly or rapidly. Thus with a mixture containing 13.5 grams gelatine per 100 cc the droplets (of solid solution) were very regularly 3μ in character when about 20 cc was allowed to cool slowly in air. Cooled rapidly, however, in an ether spray, the droplets were so minute as barely to be visible with a magnification of 400 diameters. The effect of the rate of cooling is the same when mixtures with a large gelatine content are used, and when, therefore, the internal phase is a fluid solution at ordinary temperatures. When cooling is very rapid the droplets are excessively minute; when it is slow they may be as large as 10μ in diameter (gelatine 36.5 percent of the mixture). One can therefore make the general statement that *the more slowly the division into two phases occurs the smaller and less curved is the surface of separation.*

The effect upon the structure of the rate at which a fresh condition is imposed upon the system is manifested in a very striking way when an already formed gel is cooled. The experiments upon the effect of temperature on the composition of the two phases in the case of the hydrogel of agar show that when heat is added to or taken away from the system the balance of the phases is altered, water, and perhaps agar, passing from the one to the other. It might be expected that this would take place solely by the passage of material across the surface which separates the two phases. The study of the ternary mixtures, however, makes it clear that a new approximate equilibrium may be reached in two distinct ways.

When a portion of the hydrogel of gelatine-water-alcohol is cooled slowly from 16° to, say 3° or 4°, one can see with the microscope no change beyond an alteration in the size of the droplets already present, that is to say, the fresh (approximate) equilibrium is attained by exchange across the surface which separates the phases. But if the cooling is rapid, say a fall of 10° in a few seconds, a secondary system of small droplets appears.

In all the mixtures which I examined these were formed in the external phase. Thus, when the concentration of gelatine in the whole mass was low, it was the fluid phase which underwent a division into secondary phases; when it was high, it was the solid phase. To put this fact in a general way, one can say that *when the hydrogel is exposed to a rapid fall of temperature the phase which lies on the convex side of the surface of separation undergoes division into two secondary phases.*[1] When the temperature is again allowed to rise these secondary phases fuse before there is any obvious change in the relation of the primary phases.

When once formed the phases have considerable stability. If the droplets are composed of a solid solution one may, by the addition of water, cause them to increase to relatively vast dimensions without their being destroyed; as they increase in size their refractive index approximates more and more to that of the external phase until finally they are lost sight of. The addition of alcohol, however, once more brings them into view and causes them to shrink. Owing to this stability once a configuration is established one has to far overstep the conditions of its formation in order to destroy it. This would account for the remarkable hysteresis observed in reversible gels. Thus a 10 percent solution of gelatine in water sets at 21° and melts again at 29.6°, and solutions of agar in water set at temperatures about 35° and melt at temperatures about 90°. Similarly with the ternary mixtures. In one holding about 35 per cent gelatine, the internal and external phases separate at 20°, but they mix again only at 65°. When water is added to a ternary mixture so as considerably to swell the droplets the system is unstable, and the two phases mix at once when it is mechanically agitated.

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[1] The formation of the secondary phases therefore occurs in that one of the primary phases which is under the lower hydrostatic pressure.

The properties of the ternary system: alcohol, gelatine, and water are the following:

I. Below a certain temperature it exists in two phases separated by a well-defined surface. The temperature at which the separation occurs depends upon the relative proportion of the components in the mixture. Increasing the proportion of gelatine raises it; as does also an increase in the proportion of alcohol. An increase in the proportion of the common solvent, water, however, lowers the temperature at which the biphasic character develops.

II. Both phases are at first fluid; with further fall in temperature one becomes solid.

III. The surface of separation is curved and discontinuous. In some cases, strictly as a secondary change, the discontinuous masses of the internal phase becomes continuous with one another.

IV. The more slowly the two phases are established the less is the surface which separates them, both in extent and in curvature.

V. The solid solution phase is formed sometimes on the concave, sometimes on the convex side of the surface of separation. The former happens when the proportion of gelatine is small, the latter when it is large.

It follows from the last (V) of these properties that a hydrogel may be built on two very different plans. It may consist of a solid mass containing spherical fluid droplets, or of solid droplets which, by hanging one to the other, form a framework in the spaces of which fluid is held. These two types present important mechanical peculiarities. The former is firm and elastic, and it maintains its structural integrity even under high pressure. The latter is much more brittle, and manifests a tendency to spontaneous shrinking, which is due to a continuous increase in the surface of contact or possibly union between droplet and droplet. These gels with an open solid framework therefore specially manifest that property of spontaneous shrinkage to which Graham applied the term "synæresis."

In the building of a hydrogel of the second type two distinct events occur. The first is the separation of droplets, which rapidly become solid; the second is the linking of these droplets together to a pattern so that they build a framework throughout the fluid phase. The first is the separation of a homogenous mass into two phases; the second is a phenomenon akin to the grouping of particles which are suspended in a fluid. It is probable that these two events are not directly connected with one another.

Binary mixtures (agar-water)

I know of no binary reversible system in which the optical characters of the two phases differ sufficiently to permit of direct microscopical investigation of the surface of separation. It is, however, easy to prove that in such a system as agar and water the property of gel building is dependent upon the appearance of two phases.

The agar which was used was prepared from commercial agar as follows. The strips were suspended in a large volume of distilled water for twenty-four hours; the water was then drained off, and a large part of the water absorbed by the strips was squeezed out by a powerful press. The strips were again suspended in distilled water, and again drained and squeezed after forty-eight hours. This washing with distilled water was continued for some weeks. The strips were then melted and the hydrosol filtered, and the filtrate allowed to set. The clear hydrogel so obtained was sliced and suspended for a further period of weeks in many changes of distilled water. In this way a colourless gel was obtained free from all foreign diffusible bodies. It was not found necessary to take precautions against micro-organisms. With the removal of the salts the agar ceased to afford them a suitable nidus.

Effects of pressure upon the hydrogel of agar

When gels containing 1 to 3 percent solids[1] are broken up and slightly squeezed by hand a fluid exudes. In order to

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[1] By this is meant 1 to 3 grams per 100 grams.

collect this fluid a screw press was made use of. The gel was cut into pieces, which were wrapped in fine cotton canvas which had been completely freed from soluble substances by treatment for months with hot and cold distilled water. The packet was then pressed in a screw press, and the large yield of fluid collected. When the fluid ceased to flow, the solid which remained in the canvas was removed to a stoppered vessel.

The fluid was found to be a solution of agar. This was proved by evaporating some after it had been thrice filtered to a small bulk, when it was found to set to a typical clear gel. The results of the study of the ternary systems give sufficient grounds for defining the expressed fluid as a solution of agar in water, and the solid which remains in the canvas a solution of water in agar. The effect of the composition of the gel and of temperature upon the distribution of the water and the agar in these two phases was determined. The percentage composition was arrived at by drying a known weight of each, and assuming that the residue was entirely composed of agar. The results which were obtained lie far outside of any error which could have been introduced by this assumption when one considers the pains which were taken to free the gels from foreign bodies. Further, in every case an examination of the dry residue was made in order to prove that it was composed of matter capable of forming with water a typical agar gel.

Experimental difficulties

The method used to separate the two phases, though at first sight crude, was found to be the most effective. The great error to be avoided is the blocking of the canvas pores by a mass of the solid phase, so that, instead of the true fluid phase, one really expresses fluid which has been forced through a membrane (pressure filtered). Owing to this error, a press, which I had specially made, and in which the piston drove the gel directly down on to a disc of canvas, proved quite useless. Very great force was necessary to express a fluid which was found to be almost pure water.

To succeed, it is necessary to avoid direct or great pressure.

The masses of gel are loosely placed in a long canvas packet, which is then deformed by pressing the ends together. The pressure necessary to yield abundant fluid is now quite small, for the solid framework of the gel is destroyed by being rubbed against the canvas, and is reduced to fine particles, while the fluid easily makes its way through the coarse pores of the canvas. Raising the pressure always expresses a fluid poor in agar, while with slight to moderate pressure the concentration of the expressed fluid, as tested by determining the solids in the yield at different stages, remained fairly constant, but always with a slight decrease as time went on.

The expressed fluid was filtered before the solids were estimated; this was found to lower the amount of solid to a very slight extent.

The following figures illustrate the variation in the composition of the fluid as the gel becomes more completely expressed:—

Successive equal quantities of expressed fluid contain dry agar in 100 cc. Temperature 14°

Experiment I	Experiment II
0.12	0.11
0.14	0.12
0.1	0.09

The mechanical pressure used to separate the phases will modify their composition by deforming the surface of separation. This error cannot be estimated.

The influence of the ratio of the masses of the two components upon the composition of the phases

Two portions of a fairly concentrated gel were taken. To one part water was added to dilute it, and both were then heated to 100°, and equal portions of each were poured into two glass-stoppered cylindrical vessels of identical shape, make, and size. The two vessels were then set aside to cool.

After forty-eight hours samples were cut from different levels in each gel, and used to determine the percentage composition.

Five hundred and eighty grams of each of the gels were then expressed. The results were as follows:—

Temperature 18°

Agar in 100 grams of the gel	Expressed fluid		Solid solution	
	Volume	Agar	Volume	Agar
grams	cc	percent	cc	percent
1.1	440	0.1	140	4.7
3.3	230	0.14	350	5.6

In another experiment:—

Temperature 15°

1.6	—	0.12	—	—
2.2	—	0.14	—	—

Thus an increase of the concentration of agar in the mixture produces an increase in the concentration of the agar in both phases. An explanation of this relation is suggested, and discussed later.

Effect of temperature upon the composition of the phases

This was determined by running a large mass of the hydrosol into a number of glass vessels of the same shape and size. Each vessel held 600 cc of the hydrosol. They were close stoppered and allowed to cool to the room temperature. After forty-eight hours they were placed in chambers of known temperature, where they were kept for five to seven days before the contents were subjected to pressure. In these experiments, as is obvious, the internal changes are those which follow on raising or lowering the temperature of the hydrogel from the air temperature. In other experiments the hydrosol was cooled down to, but not below, the temperature of observation. This distinction is important, because it was found that the composition of the phases varied for a given temperature according to whether that temperature was the lowest of a descending series or the highest of an ascending series. This is shown clearly in the two curves AB AB′, Fig. 1. The arrows indicate the direction, ascending or descending, of the changes of temperature.

No. 1.—Agar content of mixture 1.6 percent

	Temperature	Agar in expressed fluid	Agar in solid
Ascending series	14°	0.14	—
	33	0.29	—
	50	0.80	—
Descending series	14	0.14	—
	33	1.10	—

No. 2.—Agar content of mixture 2.23 percent

	Temperature	Agar in expressed fluid	Agar in solid
Ascending series	13°	0.12	4.7
	36	0.25	5.0
Descending series	5	0.09	3.0
	13	0.12	4.7
	36	0.47	3.2

Putting on one side for a moment the different effect of an ascending or a descending temperature change, these experiments show that (1) a hydrogel of agar is a structure formed of a more solid part and a fluid, and (2) each of these two phases is a mixture of agar and water, (3) the composition of the phases is dependent to a lesser degree upon the ratio of agar to water in the entire mass, to a greater degree upon the temperature.

While recognizing as fully as possible that only an approximation to the actual composition of the two phases at different temperatures is obtained by these experiments, it is obvious that they afford reliable information on two points. These are, firstly, the marked "lagging" action or passive resistance to change offered by the system agar-water. The difference in composition of the phases according to whether any given temperature lies in an ascending or a descending series shows how slow the system is in reaching final equilibrium.[1] Secondly, the experimental results seem to me to indicate pretty clearly the general form of a part of the concentration temperature curve. I give the curve as it appears from the figures in Experiment II. AB and CD are the curves for the system—solution of agar in water, solution of water in agar, and vapor. If they correctly represent the general form of the curve, then, by the theorem of Le Chatelier, it follows that the change from the system solution of water in agar and vapor to the system solution of water in agar, solution of agar in water, and vapor will be accompanied by a liber-

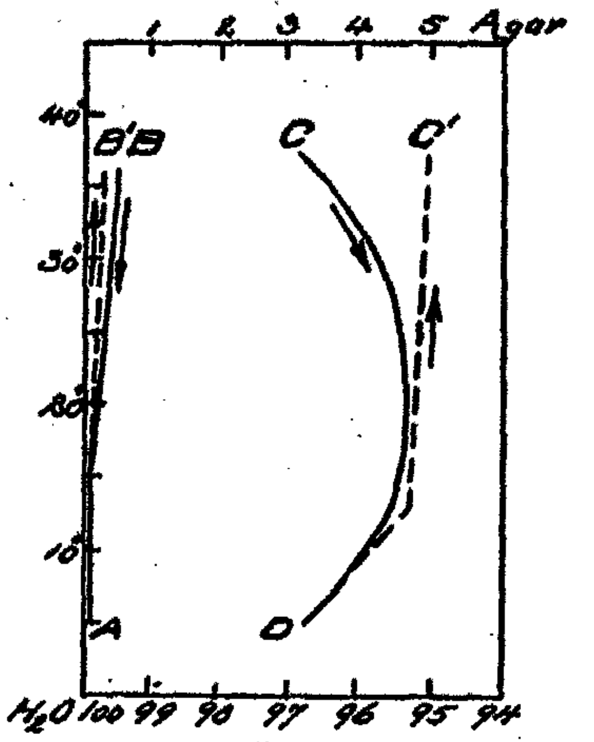

Fig. 1

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[1] The system salicylic acid and water, and thorium sulphate and water are perhaps comparable cases. The former readily yields two fluid phases which, however, are throughout in labile equilibrium (Bancroft, 'The Phase Rule,' p. 105). In the case of the latter system supersaturated solutions can be obtained over a wide range of temperatures, and even in presence of the stable hydrates it is often hours or days before equilibrium is reached (Bancroft, loc. cit., p. 54, or Roozeboom, Zeit. phys. Chem, 5, 198 (1890). The lagging action in colloids which is so markedly shown by van Bemmelen's researches into the effect of time on the hydrogel of silicic acid, ceases to be extraordinary when one remembers that one of the phases is a solid. Gels reach equilibrium much more rapidly than does, for instance, a bar of metal in which the reaction velocity is so slow that final equilibrium may never be reached.

ation of heat when the change takes place along the isotherms from 5° to ± 20°, and by an absorption of heat when the change is along the isotherms ± 20° to 35°, while the change from the system solution of agar in water and vapor to the system of two solutions and vapor will always be accompanied by absorption of heat.

I have not established this deduction experimentally, but it finds a considerable amount of support in the following facts. When water is allowed to dissolve in pure dry agar at 14°, a considerable amount of heat is given off. 1 cc of dry agar in coarse powder added to 10 cc of water gives a rise of more than 6°,[1] while control experiments with carefully dried finest graphite or sand gave a rise of temperature of 0.15° and 0.17° respectively. Wiedemann and Lüdeking[2] also found that when dried gelatine absorbs water heat is liberated, but when gelatine saturated with water is dissolved in water heat is absorbed.

I have verified the general form of the curve AB in a way which eliminates all the errors due to the expression of the fluid phase from the gel. A cylindrical column of gel 15 cm high was divided by two vertical cuts at right angles into four equal pieces. Four stoppered glass vessels were taken of the same size and shape, and in each, one of the pieces was placed and just covered with water. Two of the bottles were kept at 14° for a week, and two at 44°; the water in both was found to have dissolved some of the agar, and to contain per 100 grams of the solution 0.50 gram and 0.12 gram of dry agar respectively.

The curves AB, DC continued upward will meet at some point which marks the consolute temperature for agar and water. I have attempted to fix this point by observing the changes in the intensity of the beam of polarized light scattered normal to the ray when parallel light is passed through a gradually cooling hydrosol. The observations, which are still in an initial stage, have so far failed to fix the point.

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[1] The mercury in the Beckmann thermometer was driven beyond the scale into the upper reservoir.

[2] Wied. Ann. 25, 145 (1885).

The study of ternary systems under the microscope makes it probable that as the curves AB, DC are continued upward they reach a point beyond which the equilibrium is no longer between a fluid solution and a solid solution, but between two fluid solutions.

The first worker to regard gelation as being due to the formation of two phases, one fluid and the other solid, was van Bemmelen.[1] He has given a suggestive discussion of the formation and structure of gels, based chiefly upon the manner in which amorphous material is precipitated from a solution, and he is led to the conclusion that "coagulation or the precipitation of a gel from a solution seem to be similar phenomena; a desolution (*Entmischung*) which forms, not two layers completely separated from one another, but

"1. A framework of a material which is in a more or less transitional state between fluid and solid, and which presents those special properties to which the term colloid is applied.

"2. A fluid which is enclosed within this framework."

Van Bemmelen, however, does not consider that these two parts can be considered as two phases in the sense of the phase rule, since there is no sharp line between them,[2] and he therefore concludes that the phase rule cannot be employed to elucidate the phenomena. This opinion is based upon a study of the equilibrium between the water content of various gels and the vapour-pressure, so patient and thorough as to give it very great weight. The curves of the equilibrium points are gradually bending lines if the dehydration of the gels is sufficiently slow, but if dehydration is relatively rapid there is a sudden change of direction (Fig. 2) when the water content is very much diminished (1 to $2H_2O$ to $1SiO_2$).

It is possible that the form of these curves does not necessarily depend upon the absence of a clear separation between the fluid and the solid portions of the gel. When one considers how small is the mutual solubility of silica and water and how slight

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[1] Zeit. anorg. Chem. **18**, 20 (1898).

[2] Ibid. **18**, 121 (1898).

therefore the influence which a given mass of silica is likely to exert upon the vapour-pressure of even a relatively small mass of water, it is probable that the form of the curve is determined more by the operation of secondary influences, such as capillary tension, which depend on the structure of the gel, than upon the direct interaction of silica and water. Capillary tension would tend to lower the vapour-pressure[1] with which the gel is in equilibrium to a greater and greater extent as the spaces in the solid framework of the gel became smaller and smaller with the decrease in the water content. The tendency to reduce the surface energy at the surface of separation of fluid and solid to a minimum, which manifests itself in the spontaneous shrinkage of some of these hydrogels, would act so as to raise the vapour-

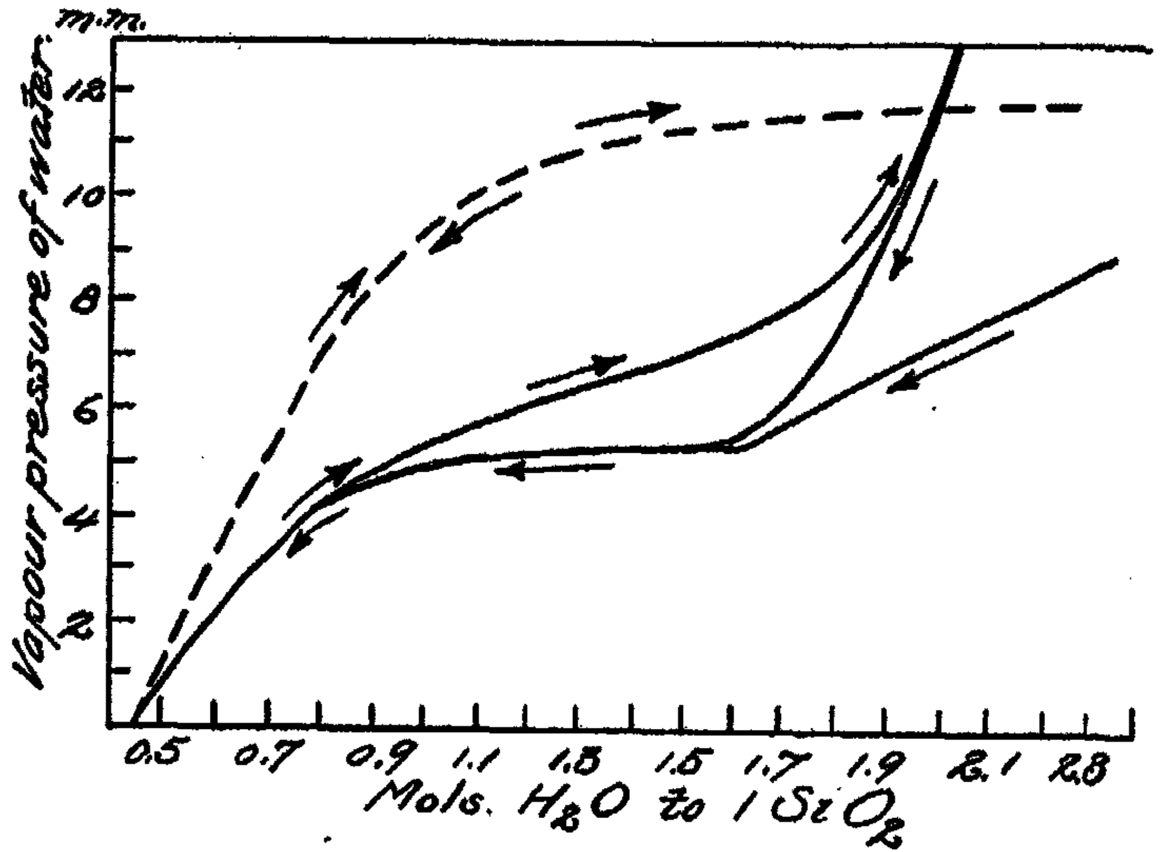

Fig. 2 (reproduced from van Bemmelen. Zeit. anorg. Chem. 13, 233 (1896).—Equilibrium between a hydrogel of silica and water vapor. Curve ...... the rate of removal of water very slow. In curve ——— much more rapid. The arrows indicate whether the curve shows the removal or the reabsorption of water.

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[1] The vapour-pressure which van Bemmelen measured is that of the free surface of the gel. It is analogous to that at the open ends of a number of capillary tubes filled with fluid.

pressure with which the gel is in equilibrium, but the operation of this factor would diminish as the surface was diminished by decrease of the water content. These two forces operating simultaneously would alone produce the characteristic gradual diminution in the vapour-pressure of the gel as the fluid component is diminished. The break in the direction of the curve when dehydration has been relatively rapid and is nearly complete is what must occur when the capillary spaces in the framework become commensurate with the masses (small spheres for instance) of solid out of which the framework is built, and when, therefore, any further diminution in the capillary spaces involves deformation of those masses, unless the removal of water is so slow that the very slow rate of readjustment in the solid phase is not exceeded. Lastly, the very limited powers of reabsorption of fluid by completely dried irreversible gels would, on this view, again not necessarily represent a reformation of the phases, that is to say, a real interaction between silica and water, but the refilling of capillary spaces by water due to the excessive capillary tension of these very minute capillaries. The capacity for reabsorption would therefore be diminished by any agent which facilitates the annealing of the dried gel and so destroys the capillary interspaces. Such an agent is heat, and van Bemmelen found that brief heating to red heat destroyed the reabsorptive powers of the gel of silica.[1]

There is one binary system in which gelation is an irreversible process (i. e. coagulation) which can be readily studied under the microscope. The hydrosol is a ternary system composed of water, a minute trace of free acid or alkali, and the modification of egg albumen which is produced by heating it to 100°. Coagulation occurs when the free acid or alkali is removed. As the coagulation point is neared the proteid particles in the hydrosol increase in size, so that spheres 0.75 to 1μ in diameter are formed. These become arranged in rows which anastomose so that an open net with regular polygonal meshes

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[1] Zeit. anorg. Chem. 13, 289 (1896).

is formed.[1] In this case the process of gel building is the same as that which can be followed so easily in ternary mixtures, and in both cases a definite surface separates the phases. It is probable that the hydrogel of silica is formed in the same way since Picton and Linder have shown by optical tests that, as the point of coagulation is approached, larger and larger particles of silica form in the hydrosol.[2] These particles may be solid solutions of water in silica, or they may be large molecular aggregates of silica free from water. I incline to think that the latter is the more probable assumption since, if they were solutions, it is difficult to see why the process should be irreversible.

In the case of the reversible systems agar-water, or gelatine-water-alcohol, the particles seem to be of the nature of solid solutions.

The system agar and water consists of two components, and, therefore, a non-variant system should be defined by four coexistent phoses. Since the gel stage consists of three phases, namely two solutions and a vapour phase, it should be a monovariant[3] system. That is to say, the composition of the phases should be fixed by fixing either the temperature, or the pressure of the vapour phase. The experiments show that this is not the case. The composition of the fluid and the solid phases is not constant for a given temperature. This result might be regarded as being due to the passive resistance to change in the system which is introduced by the formation of a solid phase. On this view, if the velocity of the reaction were known, the phases would be fixed if the element of time were introduced and accorded a definite finite value. This is the method which Bancroft suggests for dealing with such cases;[4] it is, however, possible that there are really more than $n + 2$ independent variables

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[1] The process is described in detail in an earlier paper by the author in the Journal of Physiology, 24, 182 (1899), and the information which the microscope affords as to the manner in which irreversible gels are built is discussed there.

[2] Jour. Chem. Soc. 61, 148 (1892).

[3] That is to say, a system having one degree of freedom.

[4] The Phase Rule, p. 234.

so that the hydrogel is not a monovariant system. In an ordinary system the independent variables are the components (*n*), temperature and pressure. Agar-water, however, is a system with two components, temperature and two pressures. This follows from the fact that the surface which separates the fluid and solid phases is curved. In point of fact the system is most closely represented by a system of two solutions separated by a membrane which is permeable by only one of the components, for while water will readily pass the surface of separation, agar, having the heavy immobile molecule characteristic of such organic bodies, will be almost unable to do so. Hence, if time be considered finite and small, the surface may practically be considered to be permeable by only one component. As Bancroft[1] points out, in a system of two solutions separated by semipermeable membrane there are two pressures and there will be $n + 3$ phases in a non-variant system when $n =$ the number of components. The hydrogel is a system of three phases and, therefore, on this view, to fix the composition, it would be necessary to fix the temperature and one pressure. This relation would probably be true if the curvature of the surface of separation could be fixed. This, however, is not the case, and in order to fix the composition of the phases it would be necessary either to fix the temperature and both pressures, that of the internal as well as of the external phase; or to fix the temperature, one pressure, and the form of the surface. Practically we can only fix the temperature and the pressure of the external phase. I have succeeded in obtaining two phases separated by a plane surface by cooling a hydrosol slowly in an electric field. This method may prove suitable if the system is able to recover from the forces operating during its formation. The method of taking known weights of dry agar and water and keeping them at constant pressure and temperature until equilibrium is obtained is simple, but unfortunately there is the fallacy that the dry agar is a preformed system. The structure of the hydrogel from which it is reproduced is not destroyed by drying, and the sys-

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[1] loc. cit.

tem tends to reform itself on the old lines by the filling of the original capillary spaces.

To sum up these remarks we may describe the hydrogel of agar as a system of three phases, a solid, a fluid, and a vapour phase. The equilibrium is determined by the chemical potential of the components in the various phases, by two pressures, and by temperature. Other operating variables are capillary tension and the energy of the surface between the fluid and solid phases. I have made no measurements to determine how soon the system reaches equilibrium, but the analogous system, gelatine and water, attains to a constant melting-point twenty-four hours after the formation of the hydrogel.[1]

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[1] Gelatinöse Lösungen, van der Heide, München, 1897.

ISOHYDRIC SOLUTIONS

BY WILDER D. BANCROFT

Starting with the assumption that all electrolytes follow the dilution law, Arrhenius[1] proved that when solutions of two acids had the same concentration of hydrogen as ion, these solutions could be mixed in any proportion without changing the degrees of dissociation of either acid. Such solutions he called isohydric, and he showed that it was not necessary for the two acids to have the same basicity, the proof being a general one applying to all acids, though the phenomenon of successive dissociation was not taken into account. Arrhenius then made, but did not prove theoretically, the following statement. "What has just been said about isohydric solutions of acids can be applied without change to other isohydric solutions which have a common ion." Acetic acid and ammonium acetate were cited as an experimental instance of this so that solutions are now called isohydric when the concentration of one of the dissociation products is the same in the two solutions. It is in this sense that I shall use the word. It will be shown in this paper that the statement of Arrhenius just quoted is too sweeping and is accurate only under certain definite limitations.

Nernst[2] has applied the conceptions of Arrhenius to dissociation in gases, pointing out that the degree of dissociation of phosphorus pentachlorid will not be altered if mixed with any number of volumes of isohydric chlorin vapor.

In a paper that has received but little attention, Storch[3]

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[1] Zeit. phys. Chem. 2, 284 (1888). Cf. also Wied. Ann. 30, 51 (1887).

[2] Theor. Chem. 2nd ed., 7, 415.

[3] Zeit. phys. Chem. 19, 16 (1896).

points out that Arrhenius's theory of isohydric solutions must be revised in case we admit that the Ostwald dilution law does not apply to all binary electrolytes. In this paper I shall take up the general question as to the conditions under which mixing isohydric solutions causes no change of dissociation. We will first consider the case of dissociation in gases, this being a simpler one than that of electrolytic dissociation because it is possible to add one of the dissociation products without adding anything else at the same time.

When phosphorus pentachlorid dissociates into phosphorus trichlorid and chlorin according to the equation

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

the formula for the equilibrium is

$$K\frac{1-x}{V} = \frac{x}{V}\cdot\frac{x}{V},$$

where $(1 - x)/V$ is the concentration of the undissociated phosphorus pentachlorid. If now we add the volume nV of isohydric chlorin, the total volume becomes $(n + 1)V$ and the total mass of chlorin $(n + 1)x$. We have then

$$K\frac{1-x}{(n+1)V} = \frac{x}{(n+1)V}\cdot\frac{(n+1)x}{(n+1)V}.$$

This reduces to the equilibrium formula and there is therefore no change of dissociation.

When hydriodic acid dissociates into hydrogen and iodin according to the equation

$$2HI \rightleftharpoons H_2 + I_2$$

the formula for equilibrium is

$$K\left(\frac{1-2x}{V}\right)^2 = \frac{x}{V}\cdot\frac{x}{V},$$

where $(1 - 2x)/V$ is the concentration of the undissociated hydriodic acid. If now we add the volume nV of isohydric hydrogen, we shall have, temporarily, the relation

$$K\left(\frac{1-2x}{(n+1)V}\right)^2 = \frac{(n+1)x}{(n+1)V}\cdot\frac{x}{(n+1)V}.$$

The factor $(n + 1)$ does not cancel out and the left-hand side of the equation is smaller than it should be for equilibrium. The dissociation will therefore be forced back.

When ammonium carbamate dissociates into ammonia and carbon dioxide, according to the equation

$$NH_4CO_2NH_2 \rightleftarrows 2NH_3 + CO_2,$$

the formula for equilibrium is

$$K\frac{1-x}{V} = \left(\frac{2x}{V}\right)^2 \cdot \frac{x}{V},$$

where $(1 - x)/V$ is the concentration of the undissociated ammonium carbamate. If now we add the volume nV of isohydric carbon dioxid, we shall have, temporarily, the relation

$$K\frac{1-x}{(n+1)V} = \left(\frac{2x}{(n+1)V}\right)^2 \cdot \frac{(n+1)x}{(n+1)V}.$$

The factor $(n + 1)$ does not cancel out and the right-hand side of the equation is smaller than it should be for equilibrium; the dissociation will therefore be increased. If, on the other hand, we add n volumes of isohydric ammonia, we shall have the relation

$$K\frac{1-x}{(n+1)V} = \left(\frac{2(n+1)x}{(n+1)V}\right)^2 \cdot \frac{x}{(n+1)V}.$$

This reduces to the equilibrium equation, so the degree of dissociation will not be changed. It is thus clear that we may get increase of dissociation, decrease of dissociation, or no change at all, depending on the equation representing dissociation and on the choice of the dissociation product to be added. It will therefore be desirable to put the whole matter in its most general form. We will suppose that we have a substance A dissociating into the substances B + C + ··· + M according to the equation

$$aA = bB + cC + \cdots + mM.$$

The equation for equilibrium will be

$$K\left(\frac{1-ax}{V}\right)^a = \left(\frac{bx}{V}\right)^b \cdot \left(\frac{cx}{V}\right)^c \cdots \left(\frac{mx}{V}\right)^m,$$

where $(1 - ax)/V$ is the concentration of undissociated A. If we add the volume nV of isohydric B we shall have, temporarily, the relation

$$K\left(\frac{1 - ax}{(n+1)V}\right)^a = \left(\frac{(n+1)bx}{(n+1)V}\right)^b \cdot \left(\frac{cx}{(n+1)V}\right)^c \cdots \left(\frac{mx}{(n+1)V}\right)^m.$$

From this we see that there will be no displacement of equilibrium when

$$a = b + c + \cdots + m - b,$$

that there will be a decrease in dissociation when

$$a > b + c + \cdots m - b,$$

and that there will be an increase in dissociation when

$$a < b + c + \cdots m - b.$$

For the case of phosphorus pentachlorid with chlorin added we have

$$1 = 1 + 1 - 1.$$

For hydriodic acid with hydrogen added we have

$$2 > 1 + 1 - 1.$$

For ammonium carbamate with carbon dioxid added we have

$$1 < 2 + 1 - 1,$$

while with ammonia added we have

$$1 = 2 + 1 - 2.$$

Another case of equilibrium where one might add an isohydric constituent is in the ester formation when we consider all the reacting substances present as vapors. The reaction is represented by the equation

$$C_2H_5OH + CH_3CO_2H \rightleftarrows CH_3CO_2C_2H_5 + H_2O,$$

while the expression for equilibrium when we start with all four constituents is

$$K\frac{A - x}{V} \cdot \frac{B - x}{V} = \frac{C + x}{V} \cdot \frac{D + x}{V}.$$

If we add the volume nV of isohydric water vapor we shall have, temporarily, the relation

$$K\frac{A-x}{(n+1)V}\cdot\frac{B-x}{(n+1)V}=\frac{C+x}{(n+1)V}\cdot\frac{(n+1)(D+x)}{(n+1)V}.$$

The factor $(n+1)$ does not cancel and the amount of ester formed will be decreased. This can be generalized for a reaction taking place according to the scheme

$$Aa + bB + \cdots mM = a_1A_1 + b_1B_1 + \cdots m_1M_1$$

as follows:

No displacement of equilibrium when

$$a+b+\cdots+m=a_1+b_1+\cdots+m_1-a_1.$$

Increase of left-hand system when

$$a+b+\cdots+m>a_1+b_1+\cdots+m_1-a_1.$$

Increase of right-hand system when

$$a+b+\cdots+m<a_1+b_1+\cdots+m_1-a_1.$$

In all these three cases it is assumed that n volumes of isohydric A_1 were added. The change in the dissociation of hydriodic acid on the addition of the volume nV of isohydric hydrogen can easily be calculated when x and n are known. Let $(1-2y)/(n+1)V$ be the concentration of undissociated hydriodic acid after equilibrium is reached. We have then the two equations

$$K\left(\frac{1-2y}{(n+1)V}\right)^2=\frac{nx+y}{(n+1)V}\cdot\frac{y}{(n+1)V}$$

$$K\left(\frac{1-2x}{V}\right)^2=\left(\frac{x}{V}\right)^2.$$

Dividing the first by the second, we eliminate K getting.

$$\left(\frac{1-2y}{1-2x}\right)^2=\frac{(nx+y)y}{x^2},$$

from which it is easy to obtain y in terms of n and x.

The matter is not so simple with ammonium carbamate in presence of the volume nV of isohydric carbon dioxid for we get

$$\frac{1-y}{1-x}=\frac{nx+y}{(n+1)^2}\cdot\frac{y^2}{x^2}$$

an equation involving the third power of y.

Passing now to systems involving electrolytic dissociation we will consider some of the cases that may arise on the assumption that the mass law formula holds, after which we can make the treatment more general by dropping this assumption. If we start with acetic acid and potassium acetate dissociating according to the scheme

$$CH_3CO_2H \rightleftharpoons CH_3C\overset{-}{O}_2 + \overset{+}{H} \text{ and } CH_3CO_2K \rightleftharpoons CH_3C\overset{-}{O}_2 + \overset{+}{K}.$$

We may write for the acid

$$K_1\frac{1-x}{V} = \frac{x}{V}\cdot\frac{x}{V}.$$

Since potassium acetate has not the same dissociation constant as acetic acid, we cannot start with equivalent quantities of the two substances in equal volumes if we wish to have the concentration of acetate as ion in the potassium acetate solution the same for a given volume of liquid as in the acetic acid solution. We must therefore write for isohydric potassium acetate the equation

$$K_2\frac{A-x}{V} = \frac{x}{V}\cdot\frac{x}{V},$$

where

$$A = \frac{K_1 + (K_2 - K_1)x}{K_2}.$$

If we add the volume nV of the potassium acetate solution to the acetic acid solution we shall have the relations

Acetic acid

$$K_1\frac{1-x}{(n+1)V} = \frac{(n+1)x}{(n+1)V}\cdot\frac{x}{(1+1)V}$$

Potassium acetate

$$K_2\frac{n(A-x)}{(n+1)V} = \frac{(n+1)x}{(n+1)V}\cdot\frac{nx}{(n+1)V}.$$

By cancelling out the factors $(n + 1)$ and n the two equations reduce to the corresponding equations for equilibrium so that the degree of dissociation of each of the electrolytes remains unchanged.

If we consider acetic acid and zinc acetate, the latter dissociating by hypothesis according to the scheme

$$(CH_3CO_2)_2Zn \rightleftarrows 2CH_3\overset{-}{CO_2} + \overset{++}{Zn},$$

we shall write

$$K_1\frac{1-x}{V} = \frac{x}{V}\cdot\frac{x}{V} \text{ and } K_2\frac{A-\frac{1}{2}x}{V} = \left(\frac{x}{V}\right)^2\cdot\frac{\frac{1}{2}x}{V},$$

where

$$A = \frac{(K_1 + K_2V)\,x - K_1x^2}{2K_2V}.$$

Adding the volume nV of zinc acetate to the acetic acid we get

Acetic acid

$$K_1\frac{1-x}{(n+1)V} = \frac{(n+1)x}{(n+1)V}$$

Zinc acetate

$$K_2\frac{n(A-\frac{1}{2}x)}{(n+1)V} = \left(\frac{(n+1)x}{(n+1)V}\right)^2\cdot\frac{\frac{1}{2}nx}{(n+1)V}.$$

By cancelling out the factors $(n + 1)$ and n the two equations reduce to the corresponding equations for equilibrium and there is therefore no change in the degree of dissociation of either salt.

If we consider solutions of zinc acetate and zinc sulfate dissociating according to the equations

$$(CH_3CO_2)_2Zn \rightleftarrows 2CH_3\overset{-}{CO_2} + \overset{++}{Zn}$$

$$ZnSO_4 \rightleftarrows \overset{++}{Zn} + \overset{--}{SO_4},$$

we shall write

$$\overset{\textbf{Zinc acetate}}{K_1\frac{1-x}{V} = \left(\frac{2x}{V}\right)^2\cdot\frac{x}{V}} \text{ and } \overset{\textbf{Zinc sulfate}}{K_2\left(\frac{A-x}{V}\right) = \frac{x}{V}\cdot\frac{x}{V}}.$$

Adding the volume n V of zinc sulfate solution to the zinc acetate we have

Zinc acetate

$$K_1\frac{1-x}{(n+1)V} = \left(\frac{2x}{(n+1)V}\right)^2\cdot\frac{(n+1)x}{(n+1)V}$$

Zinc sulfate

$$K\frac{n(A-x)}{(n+1)V} = \frac{(n+1)x}{(n+1)V}\cdot\frac{nx}{(n+1)V}.$$

The factor $n + 1$ cancels out in the zinc sulfate equation but does not in the zinc acetate equation. There will therefore be increasing dissociation of zinc acetate, and, as a secondary phenomenon, decreasing dissociation of zinc sulfate. This is the case that Arrhenius overlooked in making his generalization, which is not to be wondered at when we remember that he was really only considering binary electrolytes, though he did not say so. Of course, sodium sulfate and zinc sulfate constitute the same case as zinc acetate and zinc sulfate. Acid sodium sulfate could be substituted for sodium sulfate if we assume the dissociation does not take place in successive stages. Of course, sodium sulfate and sodium chlorid will be analogous to zinc acetate and zinc chlorid. On the other hand, sodium sulfate and sodium oxalate come under another head. If we have

$$Na_2SO_4 \rightleftarrows 2\overset{+}{Na} + \overset{--}{SO_4} \text{ and } Na_2C_2O_4 \rightleftarrows 2\overset{+}{Na} + \overset{--}{C_2O_4},$$

and if we write for equilibrium

$$K_1 \frac{1-x}{V} = \left(\frac{2x}{V}\right)^2 \frac{x}{V} \quad \text{and} \quad K_2 \frac{A-x}{V} = \left(\frac{2x}{V}\right)^2 \cdot \frac{x}{V}.$$

we shall have, on adding the volume nV of sodium oxalate,

Sodium sulfate

$$K_1 \frac{1-x}{(n+1)V} = \left(\frac{(n+1)2x}{(n+1)V}\right)^2 \cdot \frac{x}{(n+1)V}$$

Sodium oxalate

$$K_2 \frac{n(A-x)}{(n+1)V} = \left(\frac{(n+1)2x}{(n+1)V}\right)^2 \cdot \frac{nx}{(n+1)V}.$$

In both equations the factor $(n + 1)$ cancels and there is therefore no change of dissociation.

If, however, we take sodium sulfate and potassium sulfate or zinc chlorid and zinc acetate, we shall find both salts tending to dissociate. If we add the volume nV of potassium sulfate to one of sodium sulfate we shall have

Sodium sulfate

$$K_1 \frac{1-x}{(n+1)V} = \left(\frac{2x}{(n+1)V}\right)^2 \cdot \frac{(n+1)x}{(n+1)V}$$

Potassium sulfate

$$K_2\frac{n(A-x)}{(n+1)V}=\left(\frac{2nx}{(n+1)V}\right)^2\cdot\frac{(n+1)x}{(n+1)V}.$$

In the first equation, the factor $(n+1)$ remains in the denominator on the right-hand side; in the second equation the factor $n/(n+1)$ remains on the right-hand side.

These relations can now be put in a general form. Suppose we have a substance A_1 dissociating into the substances B_1, C_1, … M_1 according to the equation[1]

$$A_1 = bB_1 + cC_1 + \dots + eM_1,$$

and a second substance A_2 dissociating into the substances B_1, C_2, … M_2 according to the equation

$$A_2 = fB_1 + gC_2 + \dots hM_2.$$

We shall then have

$$K_1\left(\frac{1-x}{V}\right)=\left(\frac{bx}{V}\right)^b\cdot\left(\frac{cx}{V}\right)^c\dots\left(\frac{ex}{V}\right)^e \text{ and}$$

$$K_2\frac{A-\frac{b}{f}x}{V}=\left(\frac{bx}{V}\right)^f\cdot\left(\frac{\frac{bg}{f}x}{V}\right)^g\dots\left(\frac{\frac{bh}{f}x}{V}\right)^h.$$

Adding the volume nV of the solution of A_2 to the solution of A_1 we get

$$K_1\frac{1-x}{(n+1)V}=\left(\frac{(n+1)bx}{(n+1)V}\right)^b\cdot\left(\frac{cx}{(n+1)V}\right)^c\dots\frac{ex}{(n+1)V}\Big)^e$$

and

$$K_2\frac{n(A-\frac{b}{f}x)}{(n+1)V}=\left(\frac{(n+1)bx}{(n+1)V}\right)^b\left(\frac{n\frac{bg}{f}x}{(n+1)V}\right)^g$$

$$\dots\left(\frac{n\frac{bh}{f}x}{(n+1)V}\right)^h.$$

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[1] The coefficients of A_1 and A_2 are taken as unity because that is the only case known in electrolytic dissociation. It is perfectly obvious that this limitation could be dispensed with if desired. Such a case would occur with the gases HI and HBr at high temperatures.

For the dissociation to remain unchanged, it is necessary that $b + c + \ldots + e - b = 1$ and $f + g + \ldots h - f = 1$. If either of these sums is greater than unity, the salt to which it refers will dissociate further; if either of these sums is less than unity the dissociation will be forced back.

We can next consider the application of the van't Hoff formula for strong electrolytes. For binary electrolytes this can be written in the form

$$KC^2_s = C^3_i \text{ or } KC_s = C^{\frac{3}{2}}_i,$$

where C_s is the concentration of the undissociated portion and C_i is the concentration of either ion. Taking the second form as the simpler, and assuming for lack of evidence to the contrary that the concentrations of all the substances as ion are raised to the same power in the equilibrium equation, we may write for hydrochloric acid

$$K_1\frac{1-x}{V} = \left(\frac{x}{V}\right)^{\frac{3}{4}} \cdot \left(\frac{x}{V}\right)^{\frac{3}{4}}$$

and for potassium chlorid

$$K_2\frac{A-x}{V} = \left(\frac{x}{V}\right)^{\frac{3}{4}} \cdot \left(\frac{x}{V}\right)^{\frac{3}{4}}.$$

Adding the volume nV of potassium chlorid to the hydrochloric acid we have

Hydrochloric acid

$$K_1\frac{1-x}{(n+1)V} = \left(\frac{x}{(n+1)V}\right)^{\frac{3}{4}} \cdot \left(\frac{(n+1)x}{(n+1)V}\right)^{\frac{3}{4}}$$

Potassium chlorid

$$K_2\frac{n(A-x)}{(n+1)V} = \left(\frac{nx}{(n+1)V}\right)^{\frac{3}{4}} \cdot \left(\frac{(n+1)x}{(n+1)V}\right)^{\frac{3}{4}}.$$

The factor $(n + 1)$ does not cancel out in either equation and the degree of dissociation of each of the salts is decreased. This result could have been deduced from the last general equation which applies here, provided we remember that in the equations for equilibrium the exponential factors do not appear also as coefficients when the electrolyte does not follow the ordinary mass formula.

If we drop the assumption that the strong electrolytes all follow the van 't Hoff formula and the weak electrolytes the Ostwald formula, we may write, with Storch[1]

$$K_1\left(\frac{1-x}{V}\right) = \left(\frac{x}{V}\right)^{B/2}\cdot\left(\frac{x}{V}\right)^{B/2} \text{ and}$$

$$K_2\left(\frac{A-x}{V}\right) = \left(\frac{x}{V}\right)^{C/2}\cdot\left(\frac{x}{V}\right)^{C/2}.$$

We shall have no change of dissociation when $B = C = 2$; when B or C is greater than two we shall have an increase of dissociation for the corresponding salt; and a decrease of dissociation when B or C is less than two. From this we see that if we mix isohydric acetic acid with isohydric hydrochloric acid, the degree of dissociation of the acetic acid will tend to remain unchanged, but the dissociation of the hydrochloric acid will be forced back and consequently, as a secondary phenomenon, the dissociation of the acetic acid will increase. The question then arises as to the extent of the change. This can be easily formulated. Let $(1 - y_1)/(n + 1)V$ be the concentration of undissociated A_1 in the mixed solutions, and $n(A - y_2)/(n + 1)V$ the concentration of undissoctated A_2. We have then the relations

$$K_1\frac{1-y_1}{(n+1)V} = \left(\frac{y_1}{(n+1)V}\right)^{B/2}\cdot\left(\frac{ny_2+y_1}{(n+1)V}\right)^{B/2}$$

$$K_2\frac{(A-y_2)n}{(n+1)V} = \left(\frac{ny_2}{(n+1)V}\right)^{C/2}\cdot\left(\frac{ny_2+y_1}{(n+1)V}\right)^{C/2}.$$

As there are only two unknown quantities in the two equations, both can be determined by a series of approximations. If it is desired to eliminate the constants K_1 and K_2, this can be accomplished by dividing these two equations by the corresponding equilibrium equations for the single salts

$$K_1\frac{1-x}{V} = \left(\frac{x}{V}\right)^{B} \text{ and } K_2\frac{A-x}{V} = \left(\frac{x}{V}\right)^{C},$$

giving the equations

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[1] Zeit. phys. Chem. 19, 13 (1895). Cf. Bancroft. Ibid. 31, 188 (1899).

$$x^B \frac{1-y_1}{1-x} = (ny_1y_2+y_1^2)^{B/2}(n+1)^{1B} \text{ and}$$

$$x^C \frac{A-y_2}{A-x} = (ny_2^2+y_1y_2)^{C/2}\frac{(n+1)^{1-C}}{n^{1-C/2}}.$$

From Kohlrausch's measurements we may conclude that potassium chlorid and sodium chlorid are both dissociated to an extent of 93.4 percent at a dilution of one hundred liters. I have calculated the change of dissociation when equal volumes of *n*/100 KCl and *n*/100 NaCl are mixed on the assumption[1] that B for potassium chlorid is 1.36 and C for sodium chlorid is 1.48. Under these conditions the dissociation of the potassium chlorid becomes about 92.0 percent and that of the sodium chlorid about 92.3 percent. According to the theory the dissociation of each of the salts is forced back over one percent, a measurable amount. If we were to assume the van 't Hoff formula for the two salts, the change of dissociation would be of the same order of magnitude. The question then arises whether such a change actually occurs. Dr. A. T. Lincoln was kind enough to test the matter for me. The specific conductivity of *n*/100 KCl at 25° was 0.001413, of *n*/100 NaCl 0.001188. The mean of these two values is 0.0013005, while the value found experimentally on mixing equal volumes of the two solutions was 0.001310. Instead of the calculated decrease of conductivity, there is an increase; small it is true, but none the less real. The value 0.001310 is, however, less than the mean of the specific conductivities of the *n*/200 solutions. Since the first part of this paper was written, but before Dr. Lincoln made his measurements, there appeared an article by Arrhenius in which he calls attention to the fact that there should be a forcing back of the dissociation, if the van' t Hoff dilution formula holds.[2] He tested this with tenth-normal solutions of potassium chlorid and ammonium chlorid. He found that the observed conductivity of the mixture was identical with the mean value obtained from the two solutions taken separately. The experiments of Lincoln

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[1] Bancroft. Zeit. phys. Chem. 31, 192 (1899).

[2] Ibid. 31, 205 (1899).

therefore confirm those of Arrhenius in that the decrease of conductivity called for by the theory does not occur. There is, however, an apparent discrepancy between the two sets of measurements, for Lincoln found an increase of dissociation in mixing, while Arrhenius showed no change of dissociation. This seeming contradiction disappears if we consider the results obtained by Jones and Knight,[1] which were published before the paper of Arrhenius appeared, though after it was written. In Table I. are given the data for potassium and ammonium chlorids at 25°, somewhat rearranged. In the first column is the dilution in liters; in the second, the molecular conductivity of potassium chlorid; in the third, the molecular conductivity of ammonium chlorid; in the fourth, the mean values from the second and third columns; in the fifth column is the molecular conductivity of ½($KCl.NH_4Cl$).

TABLE I

Temperature 25°

V	KCl	NH_4Cl	Mean	½$KClNH_4Cl$
1	104.1	99.3	101.7	97.5
2	108.6	104.9	106.8	104.2
4	111.2	110.4	110.8	110.5
8	116.5	115.8	116.2	115.9
16	121.5	120.9	121.2	120.6
32	125.4	125.3	125.4	123.0
40	125.7	127.6	126.7	127.2
80	128.5	131.8	130.2	131.2
160	131.1	134.2	132.7	133.5
320	132.1	136.8	134.5	136.6
640	133.9	138.1	136.0	139.6

While it is not strictly legitimate to consider equivalent solutions of potassium and ammonium chlorids as always isohydric, such an assumption will introduce no serious error in the present discussion. Comparing the fourth and fifth columns we see that the values in the fourth are larger than the corresponding values of the fifth for the higher concentrations and smaller for the more

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[1] Am. Chem. Jour. 22, 125 (1899).

dilute solutions. In other words, we have an apparent forcing back of the dissociation when we mix concentrated solutions, and an apparent increase of dissociation when we mix dilute solutions. The increase in dissociation is so marked, if we may trust the experiments, that we should apparently get an increase in the dissociation of *n*/640 potassium chlorid on adding an equivalent quantity of solid ammonium chlorid. For *n*/8 solutions, the difference between the fourth and fifth columns is less than one-third of one percent, which agrees well with the values of Arrhenius for tenth-normal solutions. For *n*/80 normal solutions the observed conductivity is higher than the mean conductivity, which agrees well with Lincoln's observations on *n*/100 solutions of potassium and sodium chlorids. The slight discrepancy between the results of Arrhenius and of Lincoln is therefore due to the different concentrations of the solutions studied.

Since it is clearly established that our present theory does not represent the facts, it becomes important to find the source of the trouble. A natural assumption would be that the strong electrolytes do follow Ostwald's dilution law and that the conductivity determinations do not give an accurate measure of the dissociation. This view is not tenable because the solutions are considered isohydric on the strength of the conductivity determinations. If we throw the latter over, the solutions are no longer necessarily isohydric, and there should therefore be a greater, not a less change of dissociation.

Arrhenius[1] advances a hypothesis which is fully as unsatisfactory as the preceding. He defines isohydric solutions as solutions containing the same concentrations of ions and asserts that these will remain unchanged when mixed, quite irrespective of the concentrations of the undissociated substances. At first sight there is something plausible about this. Equal concentrations of ions or equal quantities of electricity per unit volume seem to stand in some vague relation to equal potentials and therefore to equilibrium. A single concrete instance will dispel the haziness which makes such a point of view possible. Suppose we mix isohydric solutions of potassium cyanid and of silver

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[1] Zeit. phys. Chem. 31, 204 (1899).

cyanid. We know that the degree of dissociation does change, and we do have to take into account the concentration, possible or actual, of the undissociated substances. Arrhenius himself brings in the dissociation constant of acetic acid when considering the equilibrium in a solution containing sodium chlorid and acetic acid. No one would claim for a moment that equivalent solutions of sodium hydroxid and hydrochloric acid could be treated as isohydric solutions. Quite apart from any theoretical considerations, the hypothesis of Arrhenius does not account for the experimental fact of an apparent increase of dissociation noticed by Jones and Knight, and confirmed by Lincoln.

What the experimental data show is that there is some factor, not yet taken into account, which brings about a greater conductivity in mixed solutions than one would otherwise expect. Now an increased conductivity may be due to one of two things, an increase in the migration velocity of one or more of the ions or an increase in the dissociation. The first alternative I shall not consider for the reason that I expect to show that there is a tendency to an increase of dissociation, and it will be time enough to consider the question of a varying migration velocity when, or if, it has been shown that the change in dissociation is not sufficient to account for the phenomena.

We will, therefore, consider what evidence there is that the third ion or the undissociated portion of the second salt should tend to increase the dissociation for the first salt. In the paper already referred to, Arrhenius[1] shows that when a solution is saturated with respect to a given salt, the concentration of the undissociated salt is decreased by the addition of salts with a common ion. Now a decrease in solubility means an increase in chemical potential as regards an unsaturated solution.[2] Therefore, adding one salt to a solution of another increases, in some cases, the chemical potential of the undissociated portion of the latter salt. If, however, the chemical potential of the undissociated salt be raised, that will disturb the equilibrium be-

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[1] Zeit. phys. Chem. 31, 225 (1899).

[2] Miller. Jour. Phys. Chem. 1, 636 (1897).

tween it and its dissociation products, causing an increase of dissociation.

In this paper it has been shown:

That the theory calls for a positive, negative or zero change, as the case may be, when isohydric solutions are mixed.

That when isohydric solutions of strong electrolytes are mixed, the resulting conductivity is greater than that required by the theory.

That the solubility experiments of Arrhenius point to an increased dissociation.

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VAPOR-PRESSURE RELATIONS IN MIXTURES OF TWO LIQUIDS, I

BY A. ERNEST TAYLOR

The object of this series of papers is to make an exhaustive study of the vapor-pressure relations which obtain in mixtures of two consolute liquids under varying conditions of temperature and pressure, the system thus far studied being that of acetone and water. A full series of measurements has been made of the boiling-points of solutions ranging in composition from pure water to pure acetone, over a wide range of pressures. The composition of the vapor given off from these solutions has also been determined, and the change of the composition with the pressure noted. Work of a similar nature has been carried on in this laboratory during the year by Dr. Carveth,[1] and in England by Lehfeldt.[2]

This first paper will consist largely of a description of the methods of work employed, the difficulties to overcome, and the precautions necessary in order to obtain accurate boiling-points.[3] Any one who has worked on ordinary boiling-point work knows how difficult it is to eliminate completely the phenomenon of superheating; and with mixtures of two volatile liquids the difficulty is greatly increased. Another important feature is the regulation of the pressure. The first measurements were made on the change of boiling-point with the change of pressure. A month or more was spent in perfecting an apparatus in which the phenomenon of superheating might, as far as possible, be elimi-

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[1] Jour. Phys. Chem. 3, 193 (1899).

[2] Phil. Mag. [5] 46, 46 (1898); 48, 215 (1899).

[3] The experimental data will be given in the second paper.

nated, and in which the pressure could be kept constant or be varied by carefully regulated increments.

The boiling-point apparatus (Fig. 1) consisted of a thick-walled, two-necked flask containing scrap platinum and garnets. Into one neck was tightly fitted, by means of a rubber stopper, a small glass adapter, 10 cm long and 2 cm in diameter, having a side arm ending in a 100 cc separatory funnel, by means of which the solution used was introduced. This separatory funnel

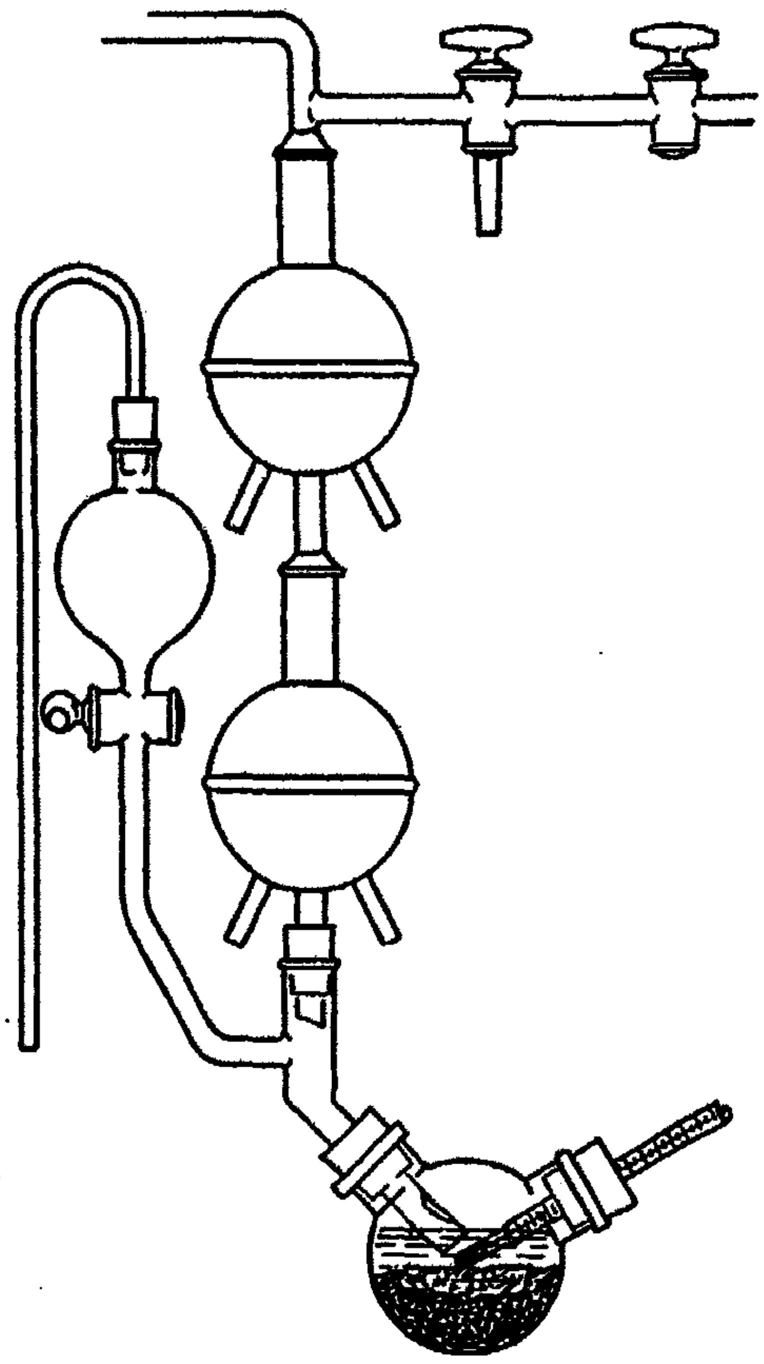

Fig. 1

was added in order that the apparatus might first be pumped out before the solution was admitted. If the solution should be added to the flask before the air was removed, evaporation would take place during the evacuation and the composition of the residual solution would be unknown. This difficulty is obviated by the use of the separatory funnel. The adapter was connected with two nickel condensers (such as used in the Beckmann boiling point apparatus) joined together by means of a tight-fitting glass tube, the joints being made air-tight, by means of a sealing-wax joint. The second condenser was connected by a similar joint to a glass T-tube, one arm of which led to a manometer, the other to a mercury pump. The separatory funnel could also connect with a Chapman pump, in which case the solution was of course not poured into the funnel until after the evacuation was complete and the connection with the water pump broken. The other neck of the flask contained a thermometer, the whole bulb of which was immersed in the liquid. This thermometer was divided into fifths of a degree and could easily be read to twentieths. It was carefully compared with a normal thermometer. The three rubber stoppers used in the adapter and in the two necks of the flasks were protected from the acetone vapors by cork stoppers about 5 mm in thickness. This simple device was found to be very effective, for as long as the rubber stoppers were kept well soaked out with water, the joints were found to hold the pressure very well. At first, and for a long time, cork stoppers smeared on the outside with a rubber cement, made from rubber and beeswax fused together, were used in place of rubber. These stoppers were fairly effective, but very troublesome.

The boiling flask of 250 cc capacity, but so filled with garnets and platinum that it would hold up to the necks only 160 cc of liquid, was warmed by means of a water-bath, in which it was immersed up to the level of the acetone solution in the flask. This water-bath, in size 23 cm x 18 cm x 10 cm, was kept at a temperature about 8° higher than that of the boiling liquid and was made of very uniform temperature by means of a funnelshaped stirrer run by a small electric motor. The source of heat was a small Bunsen burner placed under the bath, and it was controlled by means of a mercury regulator in the bath. To prevent as far as possible the radiation of heat to the apparatus above, the bath was covered by a thick sheet of asbestos. In a series of measurements, the temperature of the bath, of course, was made to vary through quite a range of temperature, and this would, if no provision against it were made, affect the temperature of the condenser somewhat, and thus make the volume of vapor vary. That the various measurements may be comparable, it is necessary that the temperature of the condensers should not change much. The water flowing through the condensers was passed through at high speed so that the vapor from the solution might be condensed as rapidly as possible. The temperature of the water, all through the winter, was very nearly constant at 4° C. It is desirable that as small an amount of vapor as possible should be given off from the liquid, and that it should be condensed quickly, for its composition is never the same as the liquid from which it is given off. For this reason the flask was filled as nearly as possible, the volume of the adapter was made small, and metal condensers of large surface were employed.

The glass tube leading to the mercury pump contained two stop-cocks about 9 cm apart, the one nearer the boiling-point apparatus being a three-way cock. Thus, when working under diminished pressure, the small space between the two taps could be shut off from the rest of the apparatus and connected with the outside air. By again turning the three-way cock, thus connecting this space with the apparatus, a small amount of air would be let in and the pressure within raised slightly. Repeating the operation as often as necessary furnished an easy means of raising the pressure slowly.

The mercury pump used was of the very simplest construction and was much the same as one described by Guglielmo.[1] It consisted of a tube 155 cm in length and 3.5 mm in bore con-

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[1] Rend. Accad. Lincei, (5) 6, II, 324 (1897).

nected with a larger tube 14 cm long and 15 mm broad. A small tube at the side of the larger tube led to the boiling-point apparatus, and another small tube at the top, furnished with a stopcock, led to a large reservoir of mercury. With this very simple pump it was found possible to lower the pressure in the whole apparatus to four or five millimeters of mercury in a few minutes (a much lower pressure than was ever necessary). The Chapman water pump used was also very effective, as the following measurements will show. One day, March 7th, when the barometer stood at 732.2 mm the apparatus was pumped out till the manometer registered a lowering of 725.5 mm, the water used being at 3.5°. The vapor-pressure of water at 3.5° is 6 mm.

When a series of measurements was to be made, the apparatus was first pumped out till the pressure was something less than 10 mm and, if possible, allowed to stand over night to test for leaks. The liquid (120 cc) was then introduced through the separatory funnel, and in consequence the pressure would rise to about 150 mm or 200 mm, according to conditions. This would bring the boiling-point somewhere between 22° and 30°, temperatures which were about as low as were practical for work. The bath, as has been stated, was kept 8° above the boiling-point. It was found well at the beginning to have the bath at about the temperature needed for the first reading. It took some little time for the apparatus to come to equilibrium, so that the reading could be depended upon, perhaps ten minutes. When equilibrium was established, a reading of temperature and pressure was made, and repeated in five minutes. During that period the pressure should not change more than one or two millimeters. Such a rate of change would introduce no inaccuracy. The thermometer readings were made to tenths of a degree, and were accurate to about that extent. With the ten percent and twenty percent acetone solutions, the limit may sometimes have been exceeded, especially at the very low pressures. These measurements under much diminished pressure are very difficult, for the boiling-point rises rapidly as the pressure on the solution is increased. In fact, all the sources of error are introduced to the most marked extent in the solutions containing small percentages of acetone. The concentration of the vapor given off, in these cases, is fully sixty percent of acetone greater than that of the boiling liquid. An accuracy of one percent can be claimed for most of the work, and of course with much of the work a greater accuracy was obtained.

When a constant pressure had been maintained for five to fifteen minutes, the pressure was gradually raised 50 mm by means of the two stop-cocks, near the mercury pump; and the temperature of the bath correspondingly raised. When equilibrium was finally reached, measurements were made as before, and so on for every fifty millimeters from 150 mm to 750 mm pressure. In cases where the rise of temperature with rise of pressure was rapid, measurements were made every twenty-five millimeters. For a final rise of fifty millimeters, it was necessary to change the pressure about thirty-five or forty millimeters, the rise in temperature of the bath doing the rest.

At first a great deal of trouble was caused by superheating. This is a most troublesome factor, for its workings are not always very evident. It is perfectly possible to obtain an apparently constant boiling-point, which may be very far from the true boiling-point. Until the effects of superheating are absolutely eliminated, one's work has little value. This source of error, however, I think that I succeeded in entirely removing. At least the inaccuracy thus introduced was not greater than my limit of error in readings. I do not feel at all sure that any one else, who has worked along this line, has obtained a boiling-point free from the effects of superheating; for I found that the ordinary methods as usually described, are wholly inadequate, in fact nearly useless. For example, I do not see how Lehfeldt could possibly obtain a correct boiling-point by simply using a piece of pumice weighted down by means of a coil of copper wire. However, he seems to be able to read his temperatures with very much more exactness than I claim for my readings.

At first I used a large amount (10 g) of scrap platinum cut into small sharp-pointed pieces. This seemed to work well enough for the first measurements, that is so long as there was air dissolved in the liquid. The different measurements made, however, did not agree well among themselves. The principal trouble came when a change of pressure was made and the liquid, in consequence, stopped boiling. On raising the temperature to bring about boiling, the liquid would become superheated; and very severe bumping would ensue, which it was impossible to prevent. Even after this bumping has been partially stopped, the liquid was sure to boil in a peculiar way characteristic of a superheated liquid, viz., in very large flat bubbles rising from the surface of the boiling liquid. The next step was to add to the platinum a large amount of garnets, so that the total volume of garnets and platinum was nearly equal to that of the liquid used. The effect was marvellous. The solution boiled in an ideal manner, small bubbles rising from all parts of the liquid. The boiling could be stopped any number of times and be again resumed even at the lowest pressures without the least trouble. Usually no effects of superheating were observed, but occasionally the liquid would boil a little irregularly for a minute or two at the beginning.

The acetone used in this work was all obtained from Roessler and Hasslacher, of Perth Amboy, N. J., and was of very good quality. It was carefully dried over calcium chloride and redistilled. The acetone thus obtained had a boiling-point of 56.0° at 740 mm pressure. From this acetone the solutions used were made by adding distilled water in varying amounts, so that a series of solutions were obtained, differing from one another by ten percent, from 0 percent acetone to 100 percent acetone. In most of the calculations afterwards, these will be reduced to molecular concentrations.

After this set of measurements to determine the vapor-pressure of mixtures of acetone and water at varying temperatures was completed, another set of measurements was made to determine the concentrations of the vapor given off under similar conditions. This, of course, required an entirely different apparatus. The work was carried out with an apparatus not very different from that used by Lehfeldt when working on the composition of mixed vapors, and was constructed as follows. As distilling flask there was used a small round bottom flask of 300 cc capacity, containing a goodly supply of garnets and scrap platinum. A three-hole rubber stopper, provided with a cork guard at the bottom, fitted in at the neck, one hole being used to admit a thermometer, the second a separatory funnel, and the third the condenser. This condenser consisted of a glass tube 9 mm in diameter directed vertically upwards from the flask for 8 cm, then bent at an angle of about sixty degrees, and after

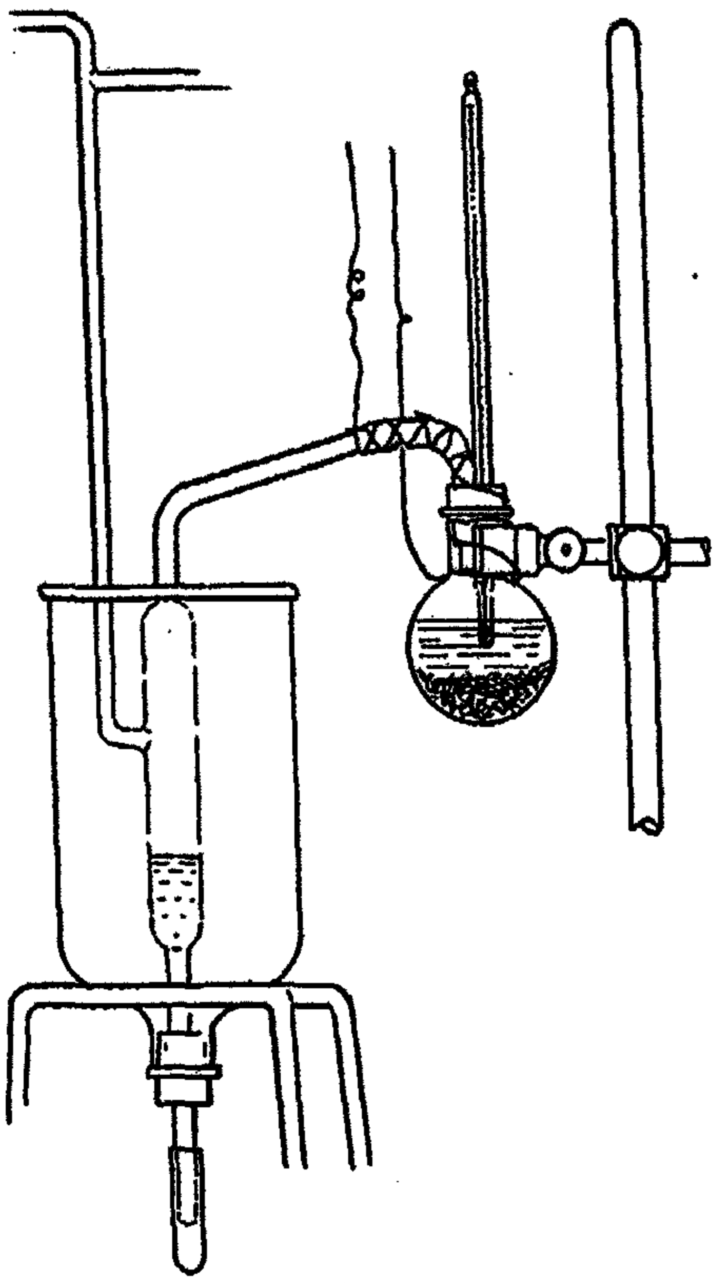

Fig. 2

about 15 cm bent directly downward, expanding into an elongated bulb of about 50 cc capacity, 20 cm long and 2 cm in diameter, terminating in a short tube 5 mm in diameter, fitted with a carefully ground glass cap. This expanded portion of the tube was surrounded by an inverted bell-jar provided at the bottom with a rubber stopper, through which the last mentioned small tube of the condenser projected, thereby making it easy, by removal of the glass cap, to empty the contents of the condenser. A small glass tube, 4 mm in diameter, bent sharply upward, was connected with the expanded portion of the condenser at a point a few centimeters above the mark which indicated that 20 cc of solution had been distilled over. This small tube ended in a T tube, one arm of which led to the condenser and the other to the manometer. The bell-jar was completely filled with a mixture of cracked ice and water, to render the condensation as complete as possible. The distilling flask, as before, was immersed in a water-bath, provided with a stirrer operated by a small electric motor. It was necessary, of course, to prevent condensation of the vapor in that part of the condenser which would allow the condensed liquid to run back into the distilling flask, otherwise the actual composition of the vapor given off would not be determined correctly, but a mixture too rich in acetone would be obtained. This was obviated by electrical heating. The distilling tube, from a point well past the first bend to the neck of the distilling flask, was wrapped in a very thin layer of asbestos (to distribute the heat) and was then wound with manganin wire, the wire continuing down the neck of the flask to the level of the liquid in the flask. By passing a current of one ampere at a potential of three volts through the wire, it was found easy to keep that part of the apparatus at a temperature which effectually prevented condensation of the vapor till it had passed the point at which it was possible for it to run back into the distilling flask.

The same solutions were used as in the previous determinations. The change of the composition of the vapor with change of pressure was found not to be very great, so each solution was distilled under but two different pressures, viz., under barometric pressure and under a pressure of about 200 mm of mercury. Two hundred and twenty cubic centimeters of solution were always used in the distilling flask, and twenty cubic centimeters distilled over into the condenser, that point being indicated by a mark. It is necessary to use an exactly known amount of solution and distill over a known amount for the concentration of the solution varies during the distillation, especially in the solutions containing the smaller amounts of acetone. The concentration at the beginning and at the end of the operation must be known and the mean used.

An actual distillation was performed as follows: The distilling flask was filled and the bath heated gradually till it reached a temperature of about three degrees higher than that at which the solution should boil, this being about the temperature necessary to make twenty cubic centimeters distill in twenty minutes. The electrical heating of the neck of the flask and the first part of the condenser was started at the same time as the heating of the bath. When twenty cubic centimeters of the distillate had been collected, it was run out into a small apparatus to determine its boiling-point and hence its composition. The distillate was made to run out smoothly without loss from spattering, by diminishing slightly the pressure in the apparatus before removing the cap at the bottom of the condenser.

In determining the boiling-point of the distillate, with care, little loss is necessary. So, in general, the distillate was put back again into the distilling flask with the solution from which it had been distilled; and the whole redistilled under diminished pressure. For solutions containing less than fifty percent of acetone a pressure of about 200 mm of mercury was used and a pressure of 250 mm of mercury for higher concentrations. If, on distilling, the pressure increased, the mercury pump was run from time to time for a few seconds to lower the pressure and thus keep it constant. As the concentration of the vapor given off varies but slightly with the pressure, it was not necessary to measure the pressure with great accuracy. When twenty cubic centimeters had been distilled over, the boiling was stopped at once by opening the three-way cock of the mercury-pump, thus raising the pressure to that of the atmosphere. When distilling at atmospheric pressure, the boiling was stopped by cooling the bath rapidly with ice water.

In the second distillation it was often difficult to start the boiling quietly, the air in the solution having been removed. A slight superheating would be produced which was liable to make the liquid boil over. After this, the liquid would boil quietly enough, but usually not until after the distillation had been thus destroyed. In either of the other pieces of apparatus, a slight superheating for a few seconds would have produced no trouble; still, the tendency toward superheating was much greater in this apparatus, undoubtedly due to the fact that the relative amount of garnets and platinum was much less than in the other cases. The trouble, however, was obviated by disconnecting the apparatus after the first distillation and raising the garnets and platinum out of the solution repeatedly, thus introducing a certain amount of air. The next two distillations were made with a fresh lot of solution, but in the reverse order, viz., first under diminished pressure and then, on putting back the distillate, under atmospheric pressure. This furnished a check on the error which might be introduced from loss of distillate.

The twenty cubic centimeters of distillate were each time carefully analyzed by determining the boiling-point in a little apparatus designed for that purpose. It consisted of a broad tube, 13 cm in width and 2.5 cm in length, blown out slightly into a small bulb at the bottom. The bulb was filled up with garnets and silver tetrahedra so that twenty cubic centimeters of solution would fill the flask very nearly up to a side arm which was attached to an ordinary glass condenser 35 cm in length. The flask was provided with a rubber stopper and cork guard through which passed, to the bottom of the solution, a so-called normal thermometer, graduated to tenths of a degree. This thermometer, No. 3060, made by Gerhardt, of Bonn, had been carefully compared by Dr. Carveth with the Reichs-Anstalt in the Department of Physics. Corrections were made, in reading the thermometer, for the height of the mercury column above the flask and for the air temperature by using the tables given for such a correction in Landolt and Börnstein's Tabellen. The solution was heated by means of a water-bath kept at constant

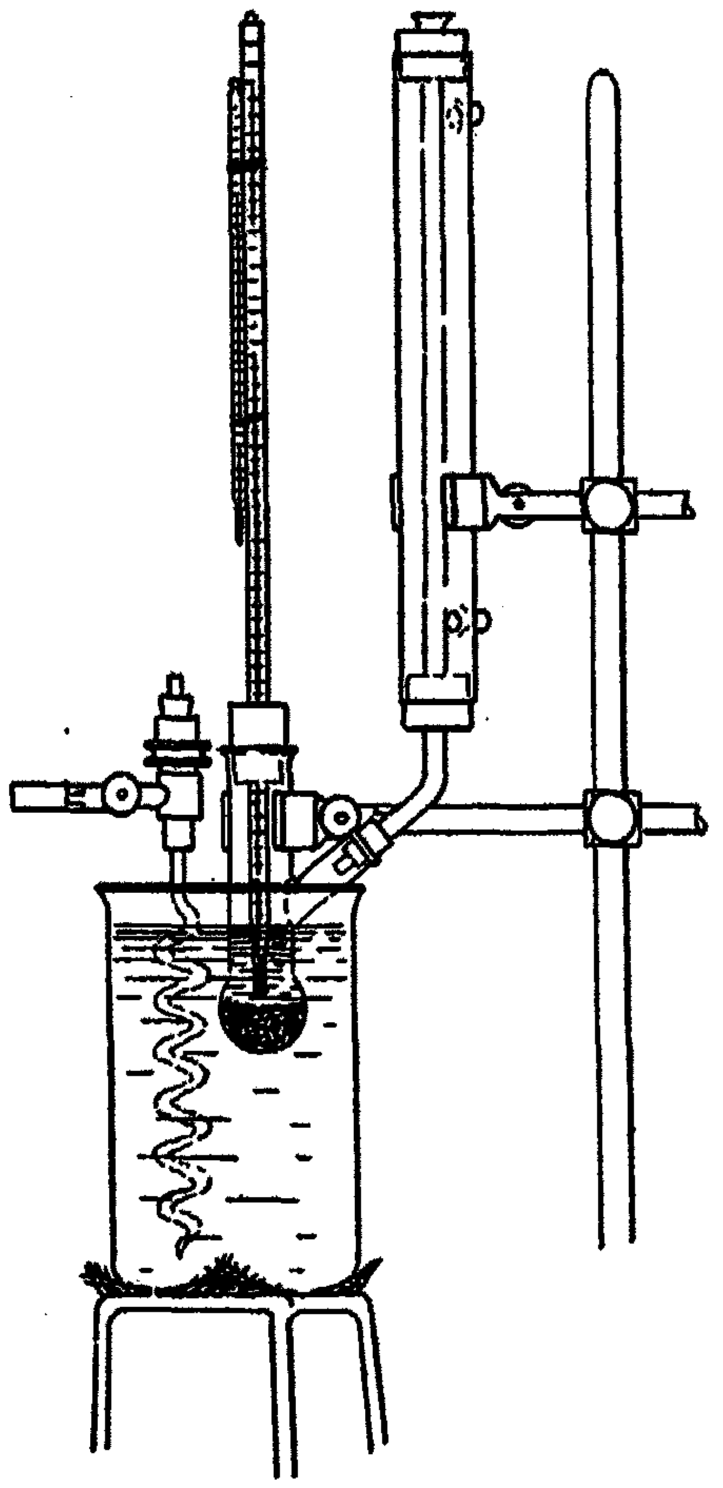

Fig. 3

temperature and very thoroughly stirred by a spiral stirrer, which was especially effective. A half liter beaker served as a water-bath.

At first, to produce constant boiling one hundred and twenty-five silver tetrahedra were used, which would seem to be a sufficient supply for twenty cubic centimeters of solution, as they have been described as especially effective. It was found, however, that the boiling-point varied with the level of the bath, with the temperature of the bath, and with the rate of stirring. In fact, a change of half a degree could be easily obtained by simply varying the temperature of the bath. It will be seen from Table I that by changing the bath seven degrees the boiling temperature is changed four-tenths of a degree. By changing the level of the liquid in the bath from the level of the silver tetrahedra to the level of the boiling liquid, the boiling-point is changed seven-tenths of a degree. In Table II the same

TABLE I

Bath at top of silver

Boiling-point	Bath temperature
57.15°	70°
57.05	67
56.95	65

Bath at top of boiling liquid

Boiling-point	Bath temperature
57.7	67
57.6	65
57.6	64
57.5	62
57.3	60

TABLE II

A. Silver tetrahedra

Boiling-point	Bath temperature
57.85°	63°
57.75	62.5
57.45	60

B. Garnets added

57·35°	60°
57·55	62.5
57·50	62.5
57·55	65

C. More garnets added

57·35°	62.5°
57·35	62.5
57·35	65
57·35	69
57·35	68

solution is taken and the level of the bath kept the same as that of the boiling liquid. In part A, the silver only is used, in B garnets are added, and in C more garnets are added till the total mass of the garnets and silver displaces ten cubic centimeters of solution, that is, their volume is just half that of the solution. In A it can be seen that raising the temperature of the bath has a marked effect, in B much less, while in C raising the temperature of the bath ten degrees above that of the boiling liquid has no effect. In Table III, other conditions remaining the same,

TABLE III

Bath at top of garnets

Boiling-point	Bath temperature
57·1+°	68°
57·1	74
57·1	75
57·1—	68
57·05	64
57·05	65
57·0	62

Bath half-way from garnets to top of liquid

57·15°	60°
57·20	63
57·20	62.5
57·25	74
57·20	72
57·20	70

Bath at top of boiling liquid	
57.35°	65°

the effect of changing the level of the bath is shown. This still has an influence, but much less; and as long as the level is the same, even a temperature twenty degrees above the boiling-point of the liquid has little effect. This shows that it is necessary to keep the bath at a constant level. Undoubtedly the level of the bath and of the boiling liquid should be the same, for if the bath reaches simply to the lower part of the interior liquid, the lower part only is boiling vigorously, while the upper part is somewhat cooled by the air and the boiling-point indicated is one or two-tenths of a degree too low. This shows very conclusively that boiling-points as ordinarily made would not be very accurate. This mixture of silver and garnets seems to be especially effective.

To determine the composition of these solutions, a series of determinations were made of solutions of known concentration from 50 percent to 100 percent acetone at various pressures, from 730 mm to 750 mm of mercury; and a curve plotted for 740 mm, the variation of the boiling-point with change of pressure being determined, and all measurements corrected to 740 mm. On determining the boiling-point of any solution of unknown concentration, and noting the barometric pressure, it was easy to read off its concentration from the curve. In all this work, the bath was kept at the level of the inside liquid.

The conclusions which I would draw from this work are as follows:

1. That without special precautions to prevent superheating, the boiling-points observed for mixed liquids are very inaccurate.

2. That often the effects of superheating may be overlooked, if conditions are not varied.

3. That when foreign substances are added to prevent superheating, they must be added in large quantities, and their volume must be at least half that of the liquid used.

4. That a mixture of platinum and garnets or silver tetrahedra and garnets is especially effective in overcoming the effects of superheating.

In conclusion, I wish to express my thanks to Professor Bancroft, for it was at his suggestion and under his direction that this work has been carried out.

Cornell University,
July, 1899

IN REPLY TO A STATEMENT MADE BY DR. E. COHEN IN A PAPER ON THE THEORY OF THE TRANSITION CELL OF THE THIRD KIND[1]

BY H. T. BARNES

In referring to the solubility determinations of zinc sulphate, made by Prof. Callendar and myself, Dr. Cohen seems to infer that we had made the assumption without verification that the salt of zinc sulphate, remaining after evaporating a solution at 100°, is the monohydrate. He cites from page 147 of our communication[2] with reference to our solutions; "They were then evaporated to dryness at 100° C, and the percentage of zinc sulphate was calculated *assuming* the residue to be the monohydrate." This is quite correct so far as it goes, but had Dr. Cohen referred back to page 141, of Section 21, of the same communication, he would have seen the following: "... We "adopted the ... method of evaporating a known weight of so-"lution to dryness at 100° C, assuming that the residue was the "monohydrate. Two determinations were made in this manner "for each solution tested, and in addition, two control experi-"ments were made in which the strength of the solution was "measured by estimating the sulphate by means of barium "chloride." Hence the statement that we had made the assumption "without proving that this was really the case by separate experiment" is quite erroneous. Moreover we endeavored to make all our measurements as accurate as we could, so that it would have been a matter of some surprise if we had overlooked this simple and obvious point.

It is exceedingly gratifying that these later determinations of the solubility of zinc sulphate given by Dr. Cohen are in such good agreement with our own.

McGill University,
March 17, 1900

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[1] Roy. Acad. Sci. Amsterdam, Jan. 24. 1900.
[2] H. L. Callendar and H. T. Barnes. Proc. Roy. Soc. 62, 117 (1897).

NEW BOOKS

The Theory of Electrolytic Dissociation and some of its Applications. *By Harry C. Jones. 14 × 20 cm; pp. xii + 289. New York: The Macmillan Co., 1900. Price: cloth, $1.60.*—The first chapter is devoted to the earlier physical chemistry, so-called, under which head come: relations between physical properties and constitution; thermochemistry; electrochemistry down to and including Kohlrausch's conductivity measurements; chemical dynamics and statics through Ostwald's affinity determinations. The second chapter introduces us to the theory of electrolytic dissociation, Pfeffer's work leading up to van 't Hoff's osmotic pressure theory, while the Arrhenius theory accounts for the exceptions. Chapter three deals with the quantitative evidence in favor of the dissociation theory; additive properties of dilute salt solutions; heats of neutralization; quantitative agreement between osmotic pressure, freezing-point, boiling-point, and conductivity measurements; dilution law; change of dissociation and solubility with a common ion; dissociation and chemical activity. The author also includes a section on the catalytic action of water vapor, though it is rather difficult to see that this is "evidence bearing upon the theory of electrolytic dissociation." In the last chapter we find the application of the theory of electrolytic dissociation to solutions, to the voltaic cell, and to biological problems.

In one or two places the text is misleading. The freezing-point constant for acetic acid comes out 38.8 only when we take 100 as the molecular weight of acetic acid; but the reader would never guess it. If this had been stated, the author would have seen that the molecular weight of the solvent as vapor is the important point theoretically and that the molecular weight of the solvent as liquid is immaterial. This is all stated clearly and accurately in van 't Hoff's original deduction, but it has disappeared from the author's version. The formula on page 143 was not deduced by Ostwald. On page 159 it should have been stated that reactions are known which do not take place between ions. On page 258 it would have been more satisfactory if the author had stated the exact facts in regard to the relation between the electromotive force of the hydrogen-oxygen gas cell and the concentration of the solution.

These mistakes are not very serious and a certain lack of perspective in regard to freezing-point and boiling-point methods is perhaps not to be wondered at. The book is readable and will probably prove useful in spite of the fact that the author splits infinitives. One point must be commented upon. The volume is partisan in tone; it presents a brief for the dissociation theory. In this, it is ten years behind the time. While the dissociation theory was still the dissociation hypothesis and was fighting for its life, it was natural and proper for the believers to lay stress upon its strong points and to slur over the difficulties. Those days are past. The outside opposition to the dissociation theory is now reduced to an insignificant guerrilla warfare. It is now time to emphasize the shortcomings of the dissociation theory, so that we may learn how to modify it, and bring it more closely in harmony with the actual facts.

Wilder D. Bancroft

Practical Methods for Determining Molecular Weights. *By Henry Biltz. Translated by Harry C. Jones and Stephen H. King. 14 × 20 cm; pp. viii + 235. Easton, Pa.: The Chemical Publishing Co., 1899. Price: cloth, $2.00.* — Under vapor densities, we have descriptions of the methods of V. Meyer, Hofman, and Dumas, together with a review of the devices for using the V. Meyer method under diminished pressure. This is followed by a discussion of the results, special attention being given to the discrepancies caused by dissociation. Half the book is devoted to the freezing-point and boiling-point methods; four pages to Nernst's method with two liquid phases; and there is a chapter on Traube's methods.

While the aim of the work is to tell how to make molecular weight determinations and not to explain the general principles of physical chemistry, the non-mathematical statement of the formulas is sufficiently complete that there is no reason why the student should not do his experiments fairly intelligently. The critical discussion of the methods is an admirable feature, but might well have been carried farther. The scrappy references to the sources of error in measuring the freezing-points of dilute solutions are not of much value. The reviewer would also have welcomed more careful comment on the effect of pressure variations on the boiling-point results. This is not asking too much because the translators have made a number of additions.

Wilder D. Bancroft

Leçons de Chimie physique. *By J. H. van 't Hoff. Translated by M. Corvisy. Part II. Chemical Statics. 16 × 25 cm; 162 pp. Paris: A. Hermann, 1899.* — The appearance of the second volume of the German edition has already been recorded (3, 946). It is a pleasure to note the promptness with which the French translation of the same volume has been run through the press. *Wilder D. Bancroft*

Optical Activity and Chemical Composition. *By H. Landolt. Translated by John McCrae. 13 × 19 cm; pp. xi + 153. (Whittaker & Co.). New York: The Macmillan Company, 1899. Price: cloth, $1.00.* — This is a translation of the eighth chapter of the first volume of Graham-Otto's "*Lehrbuch der Chemie*" (3, 110) which in its turn was abstracted from Landolt's "*Das optische Drehungsvermögen organischer Substanzen und dessen praktische Anwendungen*," (2, 196). This translation makes a very serviceable little volume, and the reviewer is happy to record the fact that the translator has used square brackets wherever he has introduced new material. This is as it should be; but it is none the less praiseworthy on that account. *Wilder D. Bancroft*

Ueber die Molekulargrösse der Körper im festem und flüssigen Aggregatszustande. *By Dr. W. Herz. (Sammlung chemischer und chemisch-technischer Vorträge.) 16 × 25 cm; pp. 377 to 420. Stuttgart: Ferdinand Enke, 1899. Price: paper, 1.20 marks.* — We have here a brief sketch of the different methods of determining molecular weights of liquids and solids, together with a statement of some of the results obtained. The author first discusses the application of the van der Waals formula to liquids, then the modifications of this by Young and by D. Berthelot. After this, we have the determinations from the vapor-pressure curve, Guye's optical method, Trouton's rule, and Liebenow's deductions from the conductivity. The surface-tension method of Eötvös and of Ramsay and Shields comes next and is followed by a discussion of Traube's hypotheses. For solids, we have Traube's relations, Liebenow's conductivity phenomena, and the behavior of solid solutions. This makes an interesting recapitulation. There is a slight lack of critical appreciation and absolutely no relation between the importance of a method and the number of pages devoted to it. *Wilder D. Bancroft*

Uber den Raum der Atome. *By J. Traube. (Sammlung chemischer und chemisch-technischer Vorträge.) Vol. 4, Nos. 7 and 8. 16 × 25 cm; pp. 255 to 332. Stuttgart: Ferdinand Enke, 1899. Price: paper, 2.40 marks.* — We have here a very interesting recapitulation of the author's hypotheses in regard to molecular weights and volumes. Whether one agrees with the author's conclusions is not to the point for the moment (2, 59). It is useful to have a given view stated in a coherent manner with references to the literature, and this the author has given us. The matter is arranged under the following heads: historical introduction; molecular solution volumes and atomic volumes of inorganic compounds and elements; molecular solution volumes, and atomic volumes of organic compounds and elements; extension of the law of Avogadro to liquids and solids; extension of the Gay-Lussac's law of gas volumes to solutions and homogeneous liquids; theory of complex compounds; the elements and the molecular co-volume; contraction law for aqueous solutions; the contraction law and the solution of van 't Hoff and Arrhenius; refraction and volume; extension of the law of Boyle and Gay-Lussac to homogeneous liquids and solids; kinetics of liquids; 'atomaric' co-volume; volume and ether; summary. This is an ambitious programme, but much is to be forgiven him who dares great deeds. *Wilder D. Bancroft*

Der Einfluss der Raumerfüllung der Atomgruppen auf der Verlauf chemischer Reaktionen. *By M. Scholtz. (Sammlung chemischer und chemisch-technischer Vorträge.) 16 × 25 cm; pp. 336 to 376. Stuttgart: Ferdinand Enke, 1899. Price: paper, 1.20 marks.* — In this pamphlet Dr. Scholtz has given a very clear and concise résumé of the influence which the contiguity of radicles may have on the reactions which take place with organic compounds. A very satisfactory account is given of the work done in this direction by Victor Meyer, Bischoff and Jacobson. *C. G. L. Wolf*

The Rise and Development of the Liquefaction of Gases. *By Willett L. Hardin. 13 × 19 cm; pp. viii + 250. New York: The Macmillan Co.,* *1899. Price: cloth, $1.50.*—The first chapter treats the early history of the subject; the second begins with the experiments of Faraday and comes down to the time of Andrews. The third chapter deals with the study of the critical point by Andrews, and with the van der Waals formula. The fourth chapter begins with the liquefaction of oxygen by Cailletet and by Pictet; this is followed by a description of the work of Wroblewski, Olszewski, and Dewar, down to 1895; next comes the liquefaction of gases by the regenerative method, and the chapter closes with a section on the liquefaction of argon, helium, hydrogen, crypton, neon, and metargon.

The book is interesting reading and the author is very non-committal when it comes to any disputed point, such as the Dewar-Hampson-Linde controversy. Perhaps this is just as well, though the reader might have been supplied more fully with references, if he is to draw his own conclusions with regard to these matters. On page 233, the author has been so carried away by his enthusiasm as to give unconsciously a false impression. There is no experimental evidence as yet that any metal will diffuse into any other metal. It is very probable that this occurs only when solid solutions are formed. The name of Cagniard de la Tour is spelled in several different ways, all of them wrong.

Wilder D. Bancroft

La Liquéfaction des Gaz. *By J. Cauro. 17 × 25 cm; p. 83. Paris: Gauthier-Villars, 1899. Price: paper, 2.75 francs.*—The first chapter deals with the general properties of gases and liquids; the second with the methods of liquefaction; and the third with machines for technical purposes. Not till the fourth chapter do we come to the scientific experiments, while the fifth chapter is divided into two parts, in one of which we find facts about the discovery of neon, crypton, and metargon, while in the other we have the commercial applications of intense cold. It is thus clear that the scope of this book is very different from that of Hardin's, while the classification is distinctly poor. The reference to Linde's apparatus for preparing liquid air is farcical.

Wilder D. Bancroft

The Compendious Manual of Qualitative Chemical Analysis of C. W. Eliot and F. H. Storer. *Nineteenth Edition. Revised by W. B. Lindsay and F. H. Storer. 13 × 19 cm; pp. vii + 202. New York: D. Van Nostrand Company, 1899. Price: cloth, $1.25 net.*—"The manual is intended to meet the wants of the general student. ... The authors have endeavored to give the student a firm hold upon the general principles and methods of the art and special pains have been taken to forewarn beginners of the errors which are most apt to mislead them."

The authors' promise to "forewarn beginners of the errors which are most apt to mislead them" has been faithfully kept. The necessity for adding reagents in proper quantity, for washing precipitates thoroughly, and for removing hydrogen sulfid, nitric acid, etc., when directed, is repeatedly exemplified; and the importance of confirmatory tests is insisted on. Very useful also are the paragraphs on the colourations produced by hydrogen sulfid, by ammonia, by ammonium sulfid; on the value of the closed test tube and of the reduction test; and on the errors to be avoided in separating Class II (Hg, Bi, Cu, Cd) from Class III (As, Sb, Sn, etc.).

"The general principles of the art" on the other hand, appear to have been understood in rather a narrow sense. Apart from the statement, "It is, in general, true that whenever, by the addition of a reagent, there can be formed in any solution a compound insoluble in the liquids present, this compound always separates as a precipitate", the principles underlying the reactions employed in qualitative analysis are passed over in silence. This omission is partially offset by a timely warning against "attempting to put a complex reaction into numerical symbols" in which case "the equations are apt to express either more than we know or less."

One hundred and five pages are taken up with an introduction and detailed instructions for the identification and separation of twenty-six metals and twenty acids. Part II (forty-three pages) treats of the systematic examination of a mixture of unknown composition, while an appendix of forty-eight pages deals with reagents, solutions of known composition, and utensils.

W. Lash Miller

Darstellung der 32 möglichen Krystallklassen, *auf Grund der Deck- und Spiegelachsen, nebst Beschreibung von Achsenmodellen zur Demonstration der Symmetrieverhältnisse der Krystalle. By H. Baumhauer. 16 × 24 cm; pp. 36. Leipzig: Wilhelm Engelmann, 1899. Price: paper, 2 marks.* — This little work is not intended to serve as an 'introduction' to crystallography; its object is to indicate a practical method of treating the subject from the modern standpoint. The reader's familiarity with crystallographic theories is taken for granted.

Of the thirty-two possible classes of crystals, thirty are possessed of axes of symmetry, while only eighteen have planes and nine a center of symmetry. The author has consequently based his argument on a classification of the axes of symmetry.

An *axis*, as defined, must not only be parallel to a possible edge of the crystal, but must be distinguishable from its neighbors by reference to the symmetry of the crystal. In this sense, the two members of the anorthic system are anaxial; while in the domatic (gonioid), an edge perpendicular to the single plane of symmetry characteristic of the class, satisfies the definition just quoted, and must therefore be considered as a *monad* axis. The axes of congruence (Deckachsen) may thus be divided into monad, dyad, triad, tetrad, and hexad; those of reflection (Spiegelachsen) into tetrad and hexad.

When an axis occurs together with plane of symmetry *parallel* to it, the axis is said to be "homogeneous"; in the opposite case, inhomogeneous. If there be a plane of symmetry *perpendicular* to the axis, the latter is termed "symmetrical", otherwise, asymmetrical. Axes of reflection are always asymmetrical.

The asymmetrical axes are further subdivided into "polar" — with unlike surfaces at each end; and "shifted" — with like surfaces, but those at one end turned with reference to those at the other, through an angle which is different for each form. It is obvious that a homogeneous axis of congruence cannot be a "shifted" axis. The surfaces at the two ends of an axis of reflection may likewise be regarded as shifted wifth reference to each other, *but all forms through the same angle* (90° or 60°, as the case may be).

The following table shows the relationship between the seven kinds of axes :

Axes of congruence (1, 2, 3, 4, 6-valent)		Axes of reflection (4, 6-valent)
(*a*) Homogeneous	symmetrical asymmetrical (polar)	(*a*) Homogeneous
(*b*) Inhomogeneous	symmetrical asymmetrical (polar or shifted)	(*b*) Inhomogeneous

If the thirty axial classes be grouped according to the *maximum* degree of symmetry of their axes, the Tetragonal and Hexagonal groups would contain seven members each and the Diagonal and Triagonal five each (corresponding to the subdivision in the table above). The five members of the Monogonal group are reduced by an investigation to one ; while the Regular group includes the remaining five classes and may be further subdivided according to the degree of symmetry of their three equal and perpendicular axes of congruence.

Twenty-one pages are devoted to a discussion of the individual classes, illustrated by a modified form of Gadolin's projection, from which it is possible to see at once

The degree of symmetry of the axes,
Whether axes of congruence or of reflection,
Whether homogeneous or inhomogeneous ; symmetrical, polar, or shifted,
The position of the faces of the most general forms,
The position of the crystallographic axes (not always axes in the author's special sense).

The simple and ingenious figures add a great deal to the value of the book, which must be regarded as an important contribution to the pedagogical side of the science.

A new set of axial models, to be had from Dr. F. Krantz, Bonn, are described in the remaining eight pages. *W. Lash Miller*

Analyse microchimique et spectroscopique. *By F. Pozzi-Escot.* (*Encyclopédie scientifique des Aide-Mémoire.*) *12 × 19 cm; 192 pp. Paris: Gauthier-Villars. Price: paper, 2.50 francs; boards, 2 francs.*—To those who believe that the possibilities of the microscope as an aid in qualitative analyses have been quite generally overlooked, it can be but gratifying to learn of the publication of another manual of microchemical analysis, since it can be taken as an indication that there is an awakening of interest in this much neglected field, and promises to arouse the interest of many in the elegant methods of microchemistry.

The little book of M. Pozzi-Escot in which 167 pages out of 192 are devoted to microchemical analysis, is in reality a condensed adaptation of Behrens' '*Anleitung z. Mikrochemischen Analyse.*' The author frankly acknowledges this in his preface.

In the first portion of the book are enumerated the various reagents and tests for the different elements, the latter being given in alphabetical order: a most unfortunate arrangement since the student is not impressed with the relations and differences existing between the elements of the different groups. The chief criticism to be made upon this section, however, is that no directions are given for applying the tests and that it is seldom that any statement is made concerning the circumstances under which the tests fail. Of the few tests given as new by the author, part are, in reality, quite old and part are of rather questionable value since they depend upon color production.

That portion of the manual dealing with the methods for the systematic examination of unknown substances is far better than the first part. The directions are clear and the discussion of sources of error good. Chemists employing microchemical methods will find this second portion of considerable value and interest. *E. M. Chamot*

Outlines of Industrial Chemistry. *By Frank Hall Thorp. 15 × 22 cm; 17 + 541 pp. New York: The Macmillan Company, 1899. Price: cloth, $3.50.* — "In this new edition, such errors as have been brought to the writer's notice have been corrected, but material changes have not been generally attempted, owing to the press of other work." The first edition having already been reviewed (3, 50) it is only necessary, in view of the quoted statement, to call attention to the early appearance of a second edition.

Wilder D. Bancroft

A Treatise on Crystallography. *By W. J. Lewis. 15 × 22 cm; pp, viii + 612. (The Cambridge University Press), New York, The Macmillan Co., 1899. Price: cloth, $3.50, net.* — Unlike the works of Groth and Mallard, the 'Treatise' of Prof. Lewis is devoted almost exclusively to the geometrical side of crystallography; though there is a short chapter (pp. 138–147) on "the systems and some of the physical characters associated with them", and, in the sections in which the systems are severally described, the importance of their physical properties in classifying various minerals is thoroughly illustrated.

Throughout the work, Miller's notation and geometrical method are adopted, the elements of symmetry being discussed as though crystals were merely polyhedra with faces subject to the law of rational indices. This method has the advantage of being remarkably free from hypotheses, but fails to establish some of the observed properties of the triad axis (p. 114) which may be accounted for by the assumption of uniformity of internal structure in crystals. The author, however, enters into this question only far enough to show the inadmissibility of pentad axes and of axes of symmetry of higher degree than six (pp. 134–137).

Great stress is laid on the methods of drawing crystals. Not only are there chapters aggregating forty pages on planes and elevations, orthographic and clinographic drawings, and linear and stereographic projection; but throughout the book there are very numerous examples of the application of these methods to special cases, with hints on the judicious selection of the axial and parametral planes, of the angles to be measured, and of the forms to be drawn first. There can be no doubt that the student would gain far more from a careful study of a number of these special cases, — crystal, treatise, and drawing board at hand, — than from the same amount of time spent in poring over a collection of models, or of minerals. The mathematical knowledge presupposed is small, analytical methods having been almost completely excluded; and the practice in mechanical drawing would be of very decided advantage to most students of 'pure' science, whose education in that respect is so markedly inferior to that of he engineers.

The Treatise is illustrated by 553 clear-cut figures. A short descriptive chapter on goniometers, and an index of sixteen columns, close the work.

W. Lash Miller

Annuaire pour l'An 1900. *Publié par le Bureau des Longitudes. 10 × 15 cm; Paris: Gauthier-Villars. Price: paper, 1.50 francs.*—We would call attention to the appearance of the edition for the present year of the familiar *Annuaire*, with its extensive collection of astronomical, physical, chemical, etc., data, and its usual special articles. The tables of data are carefully annotated by such authorities as Loewy, Cornu, and Berthelot. In the present volume, the tables of thermochemical data are replaced by a paper by Cornu on electrochemical equivalents and electrolysis. The special articles are: Machines for developing Electric Currents, by Cornu; The new Gases of the Atmosphere, by Lippmann; The Work of the Mont Blanc Observatory in 1899, by Janssen; and The Application of Aeronautics to astronomical Problems, by Janssen. A new feature is the numbering of the hours of the day from 0 to 24; thus "one dines at 19 o'clock, and goes to the theatre at half-past 20." *J. E. Trevor*

REVIEWS

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

General

Derivatives and atomic mass of palladium. *W. L. Hardin. Jour. Am. Chem. Soc.* 21, *943* (*1899*). — The author has determined the amount of palladium in diphenyl-pallad-diammonium chlorid, in diphenyl-pallad-diammonium bromid, and in ammonium palladium bromid. From these data he concludes that 107.014 is the most probable value for the combining weight of palladium.
W. D. B.

The relation of physical chemistry to technical chemistry. *W. D. Bancroft. Jour. Am. Chem. Soc.* 21, *1101* (*1899*). — Reasons are given for the assumption that a training in physical chemistry is the best training for a technical chemist. *W. D. B.*

An electric drying oven. *T. W. Richards. Am. Chem. Jour.* 22, *45* (*1899*). — A platinum wire five meters long and 0.2 mm in diameter is connected with a fifty-volt circuit. A glass or porcelain cylinder jacketed with asbestos is placed above the resistance frame, while the top is partially closed by an inverted dish or watch-glass. In order to insure uniform temperature, a stationary mica fan is placed just over the resistance frame to distribute the rising current of hot air. [Now that thoroughly satisfactory motors can be bought for a dollar and pretty fair ones for half that price, it would seem better to introduce an efficient stirrer]. *W. D. B.*

A simplification of Beckmann's boiling-point apparatus. *S. L. Bigelow. Am. Chem. Jour.* 22, *280* (*1899*). — The author does away with the external heating and the internal devices for preventing superheating, such as beads and platinum, and uses, as the source of heat, a fine platinum wire through which a current is passed. It is assumed that superheating is done away with, though the fact that the current must be kept constant militates against this assumption. The fact that constant readings are obtained for constant current does not prove that the readings are right, and it is by no means certain that the amount of superheating is the same with the pure solvent as with the pure solution. The method is in the line of improvement, however, and these criticisms do not really bear upon its use as in elementary laboratory work; but rather against its being considered as really accurate in its present form. *W. D. B.*

A method for carrying out chemical reactions under high pressures. *B. H. Hite. Am. Chem. Jour.* 22, *80* (*1899*).—A platinum tube is filled with the solution of the reagents closed with a stopper or screw cap, and placed in a lead tube. The lead tube is then closed with a lid and placed in a steel cylinder which has a hole through it about 1.25 inches in diameter.

The lead tube rests on a steel plug, which closes the lower end of the cylinder and rests on the bed-plate of a powerful hydraulic press, while the pressure exerted by the ram of the press is communicated by a steel piston to the lead tube and its contents. The platinum tube simply serves to separate the reagents within from the water surrounding it. The lead tube is securely sealed by the pressure so that the liquid is completely encased in one continuous piece of metal. If pressures of 200,000 pounds to the square inch are desired, a cylinder with 0.75 in. bore should be used. With a cylinder having a 0.5 in. bore, pressures of over 400,000 pounds to the square inch have been obtained, but in such tests the tool steel pistons were completely crushed. *W. D. B.*

A dissolver. *A. J. Hopkins. Am. Chem. Jour.* 22, *407* (*1899*).—In order to avoid a mechanical stirrer, the author arranges a combination of glass tubes in a cylinder in such a way that when connected with a water pump it sucks up saturated solution from the bottom of the cylinder and produces an effective stirring. *W. D. B.*

One-Component Systems

The preparation of pure tellurium. *J. F. Norris, H. Fay and D. W. Edgerly. Am. Chem. Jour.* 23, *105* (*1900*).—Tellurium was prepared from the basic nitrate and a study of this compound was made. To test the question as to the homogeneity of tellurium, the double bromid of potassium and tellurium was submitted to fractional crystallization. The slight difference between the end-products is considered by the authors not to exceed the experimental error in the analysis. *W. D. B.*

Observations upon tungsten. *Edgar F. Smith. Jour. Am. Chem. Soc.* 21, *1007* (*1899*).—When sulfur monochlorid acts upon tungsten trioxid, the product formed is the oxychlorid $WOCl_4$. All attempts to prepare tungsten alkyls proved unsuccessful. It was also found impossible to isolate any esters of tungstic acid in a pure state. The trioxid occurs in two forms, a soluble and an insoluble one. These have different though unknown densities, and are mutually convertible, though the conditions have not been worked out in a satisfactory way. No really satisfactory method has yet been found for determining the combining weight of tungsten. Provisionally, it would seem advisable to call it 184. *W. D. B.*

Application of liquid hydrogen to the production of high vacua, together with their spectroscopic examination. *J. Dewar. Proc. Roy. Soc.* 64, *231*; *Ann. Chim. Phys.* (*7*) 17, *12* (*1899*).—On cooling a tube with liquid hydrogen, practically all the gas in the tube is condensed and a very high vacuum is thus reached very rapidly. This has been confirmed experimentally. *W. D. B.*

The latent heat of fusion of naphtylamin and of diphenylamin as related to the molecular cryoscopic depressions in these solvents. *J. M. Stillman and R.*

E. Swain. Zeit. phys. Chem. 29, *705* (*1899*). — The latent heat of fusion of naphtylamin was found to be 25.59, that of diphenylamin 23.97; the melting-points of these substances were ascertained to be 50.1° and 54° respectively. When these values are substituted in van 't Hoff's formula, $K = \frac{1.991T^2}{w}$ the molecular cryoscopic depressions of naphtylamin and diphenylamin are found to be 81.2 and 88.8 respectively. According to Eykman's cryoscopic determinations, these constants are 78 and 58 respectively. The agreement is very much better than that obtained when Battelli's determinations of the latent heats of fusion are used. *L. K.*

On the alteration of the thermal conductivity by fusion. *E. van Aubel. Zeit. phys. Chem.* 30, *563* (*1899*). — In view of the fact that several substances (salts) show no sudden change in heat conductivity at the melting-point, the author points out that in the case of water a very marked decrease in conductivity occurs when water freezes. *F. B. K.*

Two-Component Systems

The freezing-point of mix-crystals of two substances. *H. W. Bakhuis Roozeboom. Zeit. phys. Chem.* 30, *385* (*1899*). — This research contains a complete qualitative account of the possible equilibria between liquid mixtures of two substances and their mix-crystals. The graphical method of van Ryn van Alkemade is adopted throughout and a number of concentration-temperature projections of the lines of contact of the ζ-surfaces with their tangential planes are given, affording a very clear insight into the changes occurring when a melt of given composition is gradually cooled. Three main divisions are considered according to whether the melts solidify to (i) a continuous series of mix-crystals of the same kind, (ii) an interrupted series of mix-crystals of the same kind, (iii) two kinds of crystals. Various types of equilibrium occur under each head, depending on the relative shapes and positions of the ζ-curves. Under (i), for instance, there are three types in which the solidification curves (conc. temp. projections above mentioned) show (1) neither maximum nor minimum, (2) a maximum, (3) a minimum. The analogy between these three types and the corresponding cases of binary equilibrium between liquid and vapor is pointed out, and conclusions completely parallel with those holding for fractional distillation are drawn regarding the possibility of separating the constituents of a melt by fractional crystallization. For all the various types, the general law holds that the content of that substance by the addition of which the melting-point is lowered is greater in the melt than in the mix-crystals. Actual cases illustrative of many of the types are mentioned as being investigated in the author's laboratory. *F. B. K.*

The transition points of mix-crystals. *H. W. Bakhuis Roozeboom. Zeit. phys. Chem.* 30, *413* (*1899*). — If, besides forming mix-crystals, the two components of a system have the additional power of existing in two or more forms, a number of distinct types of transition points will exist. The author restricts himself to the cases in which not more than one transition temperature exists for each component and assumes that if the two substances in one state (α) form mix-crystals with each other, they will be more or less miscible in their second state (β) also. The treatment is exactly similar to that in the above article. The classifications of the various types of transition is based on the way in which the melt first crystallizes on cooling, and consists of three main divisions, identical with i, ii, and iii of the preceding research (see above). In division ii there occur four types. The condition for one of them (IV) is that the mix-crystals in both stages (α and β) form a discontinuous series. The following research deals with an example of this type of transition. *F. B. K.*

The formation and transformations of the mix-crystals of potassium and thallium nitrates. *C. van Eyk. Zeit. phys. Chem.* 30, *430* (*1899*). — Both potassium and thallium nitrates are dimorphous, the pure salts having transition points at 129.5° and 144.3° respectively, both of which temperatures are lowered by the addition of the other substance. At the higher temperature, both salts are rhombohedral; at the lower they are rhombic. In both states the substances form a discontinuous series of mix-crystals. The case, therefore, is representative of the type IV (above review). By a careful series of analyses of melts and mix-crystals and by determination of transition points of the solids by thermometric and optical methods, the author has constructed a complete diagram showing the transition points for all possible mixtures of KNO_3 and $TlNO_3$ and fulfilling all Roozeboom's predictions regarding this type of equilibrium.

F. B. K.

The change of the inversion point of ammonium nitrate at 32° on addition of potassium nitrate. *W. Müller. Zeit. phys. Chem.* 31, *354* (*1899*). — Addition of potassium nitrate to a saturated solution of ammonium nitrate in water lowers the inversion point. From the quantitative change of the inversion and the relative concentrations, the author concludes that the molecular weight of potassium nitrate in the solid solution below the inversion point is three-fourths that of potassium nitrate in the solid solution above the inversion point. The corollary is that above 32° solid ammonium nitrate has a molecular weight equal to three times the formula weight, while below 32° it is four times the formula weight. A simpler conclusion would be that the difference between three-fourths and unity is due to defective theory and that the molecular weight of solid ammonium nitrate undergoes no change at the inversion point.

W. D. B.

On the stable hydrates of manganese chlorid above 0°. *H. M. Dawson and P. Williams. Zeit. phys. Chem.* 31, *59* (*1899*). — Between 198° and 57.9° $MnCl_2 2H_2O$ crystallizes as stable form from the solution; between 57.9° and – 2° $MnCl_2 4H_2O\ \alpha$ can exist in stable equilibrium with the solution. Below – 2° the hexahydrate separates. There is also a second tetrahydrate, $MnCl_2 4H_2O\ \beta$, which is not the stable form at any temperature. *W. D. B.*

On the solubility of organic acid anhydrids. *E. van de Stadt. Zeit. phys. Chem.* 31, *250* (*1899*). — When succinic anhydrid is shaken with water at 0° the amount of substance going into solution increases for a while, passes through a maximum, and then falls to a little more than one-half the maximum value, the solution then being saturated with respect to succinic acid. The explanation is very simple. Succinic anhydrid dissolves as such and is nearly twice as soluble as succinic acid. In the course of time, it takes up water, forming succinic acid. A similar, though less sharply marked, phenomenon was observed with phthalic anhydrid. *W. D. B.*

On the influence of the nature of the solvent upon the cryoscopic behavior of phenols. *K. Auwers. Zeit. phys. Chem.* 30, *300* (*1899*). — Substances showing an abnormal cryoscopic behavior can be classed under two heads: (1) those which tend with increasing concentration towards a limit corresponding to double the theoretical molecular weight, and (2) those whose "cryoscopic molecular weight" increases apparently without limit with increasing concentration. For the second class of substances, which includes alcohols, phenols and acid amids, the association hypothesis supplies no very satisfactory explanation; the author therefore suggests the possibility of a mutual action between solvent and solute. The investigation was undertaken with the idea of bringing out relationships between these abnormal results and the properties of the solvent. The method was to study the behavior of substances one at a time in a number of different solvents. The resultant values show that no connection exists between either the melting-point or the depression constant of the solvent and its behavior, but apparently the presence of certain substituting groups has a very marked influence. Thus it is found that *p*-nitrophenol, while giving almost normal values in aromatic nitro-compounds, behaves very abnormally in the corresponding halogen derivatives, and the same holds for other solutes.

A. P. S.

Cryoscopic investigations on the constitution of the amids. *K. Auwers. Zeit. phys. Chem.* 30,*529* (*1899*).—The author attempts to decide the constitution of the amids by the consideration of the abnormalities in the molecular lowering of freezing-point. The presence of either the group $-OH$ or $-NHC_6H_5$ may cause abnormality. Negative groups such as $-NO_2$ on the other hand tend to lessen or nullify the abnormality, but only when they are attached to the carbon atom next to the one with the $-OH$ group. Experiments on a number of ortho-substituted benzanilids show that the abnormality is nullified only when the negative substituting group is in the basic half of the molecule from which the author concludes that the amids, assuming that they are constituted alike, contain the group $-NHC_4H_5$ and not $-OH$. *F. B. K.*

On the nature of the so-called colloidal solutions of the metals. *K. Stoeckl and L. Vanino. Zeit. phys. Chem.* 30, *98* (*1899*). — Colloidal solutions of some of the metals have been known for a considerable time; gold, silver, bismuth, and, most recently, mercury, have thus been produced in a condition of pseudo-solubility. The present investigation was undertaken for the purpose of determining whether such preparations can be correctly called solutions, or are merely cases of suspension.

As a result, the authors find that they do possess all the physical properties of suspensions and none which require any other assumption to be made about them.

The evidence obtained from a study of the preparations of gold, is as follows: animal charcoal separates the gold completely; freezing out does the same.

The test devised by Muthmann shows that when a solution of gum arabic is added to a colloidal gold solution and the gum then thrown down by addition of alcohol, it carries with it all the gold. On redissolving in water a solution of the original character is again obtained. When the solutions are heated complete precipitation is brought about, owing to the massing together of the small particles as they are carried about by convection currents. With regard to the optical behavior—one of the best tests—these so-called solutions have the power of polarizing transmitted light, a property characteristic of all suspensions. On passing an electric current through the solution, the gold particles are negatively charged by friction with the water and flow to the positive pole.

The authors devote a good deal of space to the explanation of the color of these solutions, and in a note at the end bring the colloidal sulfid solutions into line with the ones studied above.

The experimental facts here brought forward are not all new, as pointed out in a later paper by Bredig and Coehn, Zeit. phys. Chem. **32**, 129 (1900).

A. P. S.

The occlusion of hydrogen by metallic cobalt and other metals. *G. P. Baxter. Am. Chem. Jour.* **22**, *351* (*1899*).—For cobalt, the author draws the conclusions:

"The volume of occluded hydrogen depends upon the amount of surface presented, which in the case of metals reduced from the oxide varies with the purity of the metal and the temperature of the reduction.

"Again, since at ordinary temperatures the occlusion of hydrogen progresses very slowly, while at the temperature of reduction 400°–500°, it amounted to an almost negligible quantity, at some intermediate temperature the occlusion must proceed at a maximum rate.

"Thirdly, the time during which the metal is in contact with the hydrogen is an important factor in determining the quantity of this gas taken up."

With nickel, copper and silver, similar results were obtained, though the total amount of hydrogen taken up by copper or by silver is very much less than in the case of cobalt.

W. D. B.

The solubility relations of argon and helium in water. *T. Estreicher. Zeit phys. Chem.* 31, *176* (*1899*).—Ramsay found 0.0394 and 0.0405 for the solubility of argon in water at 12° and 13.9°. The author, working in Ramsay's laboratory, finds 0.04375 and 0.04145 at the same temperatures. For helium the author finds 0.01396 at 15° and 0.0138 at 20° as against Ramsay's preliminary value of 0.0073 at 18.2°. The solubility of helium passes through a minimum at about 25°. Below 30° it is less soluble than nitrogen, above 30° more soluble.

W. D. B.

The electrolytic dissociation of certain salts in methyl and ethyl alcohols, as measured by the boiling-point method. *H. C. Jones. Zeit. phys. Chem.* 31, *114* (*1899*).—The apparatus was the one devised by the author (1, 743). Tenth-normal solutions of potassium, sodium, and ammonium bromids and iodids show 50–60 percent dissociation in methyl alcohol and 20–30 percent dissociation in ethyl alcohol. Potassium and sodium acetates of the same concentration are about thirty-seven percent dissociated in methyl alcohol and about fifteen percent dissociated in ethyl alcohol.

W. D. B.

Some boiling-point curves, II. *J. K. Haywood. Jour. Am. Chem. Soc.* **21**, *994* (*1899*). — The author has determined boiling-point curves for mixtures of benzene with chloroform, carbon tetrachlorid, ether, acetone, and methyl alcohol; also for mixtures of methyl alcohol with ethyl alcohol, carbon tetrachlorid and ether. Minimum boiling-points were obtained with benzene and methyl alcohol, with methyl alcohol and carbon tetrachlorid. The generalizations previously made (3, 317) still hold good. *W. D. B.*

A contribution to the study of liquid mixtures of constant boiling-point. *G. Ryland. Am. Chem. Jour.* **22**, *384* (*1899*). — Out of eighty pairs of liquids studied, forty-five gave a minimum boiling-point, and two a maximum boiling-point. The author's theoretical views are painfully elementary and some of his experimental work is not above suspicion. *W. D. B.*

The variations from Boyle's law with mixtures of hydrogen and carbon dioxid. *J. E. Verschaffelt. Zeit. phys. Chem.* **31**, *97* (*1899*). — When hydrogen and carbon dioxid are mixed, the resulting pressure is higher than that calculated. The author has computed the constants for formulas of the van der Waals type for the different relative concentrations of the two gases. *W. D. B.*

Thermal effects of the dilution of some salts. *F. P. Dunnington and T. Hoggard. Am. Chem. Jour.* **22**, *207* (*1899*). — The authors have determined the heat effects when successive additions of water are made to concentrated solutions of seventeen different salts. *W. D. B.*

Poly-Component Systems

Equilibria in the system: water, phenol and anilin, II. *F. A. H. Schreinemakers. Zeit. phys. Chem.* 30, *460* (*1899*). — The present is the third instance of equilibrium in a system of three components, *A*, *B* and *C*, where two liquid phases exist in the binary systems *AB* and *AC* but not in *BC*. In the first case [water *A*, benzoic acid *B*, and succinonitrile *C* (3, 565)] the limits of temperature within which two liquid phases are found in the system *AB* (96°–115° C) are quite different from those in *AC* (18°–56°); in the second [succinonitrile *A*, water *B* and alcohol *C*, two liquid phases in system *AB* from 18°–56° and in *AC* from 13° to 51°, (3, 565)], and in the third [water *A*, phenol *B* and anilin *C*, 15°–68° in *AB*, —0.5° —167° in *AC*] the two pairs of liquid phases may be observed at the same temperature. And while in the second instance a study of the ternary system reveals two entirely separate sets of heterogeneous systems (two binodal curves) in the third this is not the case. Only one binodal curve exists which from 15° to 68° stretches across the diagram from the side *AB* to the side *AC*. The third instance is moreover characterized by the occurrence of a binary compound $C_6H_5NH_2.HOC_6H_5$ melting at 31° C.

After a paragraph on each of the three binary systems, the author describes experiments leading to the construction of the usual three-dimensional diagram, of which many of the other figures in the article may be regarded as projections.

Ten pages are devoted to a discussion of the "curves of maximum temperature" (M curves), whose ordinates give the highest temperatures at which a pair of liquid phases can be obtained, by adding the third component to a mixture containing the other two in the proportions given by the abscissæ. The points on the M curves may be determined by drawing tangents from the corners of the triangular diagram to the binodal curve, the direction of the tangent giving the abscissa and the temperature represented by the diagram the ordinate of the point.

Stress is laid on the distinction between these M curves and the plaitpoint curves (or curves of critical solutions), which, for each temperature, give the composition of the system in which the two liquid phases become identical.

F. B. K.

On reciprocal salt pairs, II. *Second paper. W. Meyerhoffer and A. B. Saunders. Zeit. phys. Chem.* 31, *370* (*1899*).—The authors call attention, as to something new, to the fact that when one of the components has a negligible vapor-pressure, the pressure-temperature curve for ice, solution and vapor coincides with that for ice and vapor. They also claim to be the first to have called attention to the difference between quadruple, quintuple, and sextuple points, which are minimum temperatures for solution and vapor, and those which are not. They then discuss the field for anhydrous sodium sulfate in systems composed of KCl, NaCl, K_2SO_4, Na_2SO_4, and H_2O, passing on to the general discussion of fields for one or more components. The measurements of Mazotto and others are taken up with special reference to the distinction between congruent and incongruent cryohydric points. One of their final conclusions is interesting, though not convincing.

"In discussing many secondary changes, covering a large field of non-volatile salts, the phase rule offers a less satisfactory point of view than the van 't Hoff conception of an inversion temperature lowered by addition of other substances."

W. D. B.

On the solubility of ethyl acetate in aqueous salt solutions. *H. Euler. Zeit. phys. Chem.* 31, *360* (*1899*).—The solubility of ethyl acetate in water is decreased by the addition of salts, and the percentage decrease appears to be a function of the solubility of the salt, being greater the more soluble the salt. So far, the author is dealing with facts; but he cannot refrain from a hypothetical conclusion that "the decrease of the solubility due to the salts and certain weak electrolytes is probably due to the volume contraction or to the increase of the internal pressure." In spite of this last conclusion, the paper is a sign of progress. The author has been determining facts instead of contenting himself with denying the existence of well-known phenomena. The physical chemistry of the last six years has been marked by a belief that facts not only should but can be ignored. The future historian will point this out as a reversal to barbarism, very surprising in the last decade of the nineteenth century.

W. D. B.

A contribution to our knowledge of dicarbonyl cuprous chloride. *W. A. Jones. Am. Chem. Jour.* 22, *287* (*1899*).—This is an admirable instance of how not to do things. The compound formed by the action of carbon monoxid on cuprous chlorid and water probably has the formula $Cu_2Cl_2 2CO.4H_2O$. The author diminishes the external pressure at constant pressure and finds that half the carbon monoxid is given off at about 135 mm and half at about 60 mm when water is present, while practically all of it goes off at about 135 mm if dilute hydrochloric acid is present. No conclusions are drawn from this. The effect of temperature was next studied, but, instead of putting in a manometer and determining the decomposition pressure, he measures the amount of gas given off at each temperature, a most hopeless waste of time. *W. D. B.*

Studies of the hydrolytic dissociation of salt solutions. *A. Ley. Zeit. phys. Chem.* 30, *193* (*1899*). — The investigation embraces a careful study of the hydrolysis of some of the salts of the metals, with the idea (1) of attempting to clear up the problem of their constitution, and (2) of determining in the light of the periodic system, the relative basicity of certain of the elements scarcely amenable to other methods of research. Three quantitative methods were employed in determining the extent of hydrolysis:

(1) The saponification of methyl acetate,
(2) The inversion of cane-sugar,
(3) Electrical conductivity.

The paper is full of interesting material, but only a few of the author's conclusions can be cited here:

In confirmation of earlier data, it is found that even the so-called neutral salts have at higher temperatures the power of inverting sugar solutions; a good reaction constant is not found in such cases.

The basicity of metallic hydroxides may be estimated from the inversion constant; in this way beryllium is found to be about eleven times more strongly basic than aluminium. The behavior of lithium salts is in accordance with the position of that element in the periodic system. Beryllium salts suffer a good deal of hydrolytic dissociation, while salts of magnesium and zinc behave almost like the typical neutral salts.

Certain mercury and cadmium salts exhibit characters which throw these elements in strong contrast, one to the other.

Aluminium salts are more strongly hydrolyzed than those of beryllium.

Since the dissociation of water increases markedly with rising temperature, changes of temperature will influence the hydrolysis of salts; this influence is shown to be very considerable in the case of aluminium chlorid. *A. P. S.*

On the nature of aqueous ammonia and amin solutions. *A. Hantzsch and F. Sebaldt. Zeit. phys. Chem.* 30, *258* (*1899*). — The method adopted by the authors for investigating the problem in hand, was to study the distribution coefficient of the compounds mentioned between different pairs of liquids, — as water and ether, water and chloroform, water and benzene, etc., — at different temperatures. Expressing by $\frac{\Delta k}{\Delta t}$ the percentage increase of the third substance in one or other of the two solvents, for a rise of 1° C, they find that the value of this expression shows very marked changes, sometimes in one direction, sometimes in another. The changes are too large, in some cases at least, to be accounted for by the increased or decreased solubility of the liquids in one another, and, the authors think, point to a change in the nature of the third substance. With trimethylamin and triethylamin the results indicate that above a certain temperature $\frac{\Delta k}{\Delta t}$ becomes 0; from this and from the abnormal behavior of other ammonia derivatives, the authors argue in favor of the assumption of the existence of hydrates of these compounds, having a temperature limit of stability. *A. P. S.*

Studies on absorption. *J. G. C. Vriens. Zeit. phys. Chem.* 37, *230* (*1899*). —Nitric acid solutions were passed through filter paper and the change of concentration determined by measuring the conductivity. The author concludes that the decrease in concentration is proportional to the number of filtrations. [It is much more probable that the percentage decrease of concentration is proportional to the number of filtrations.] *W. D. B.*

A demonstration of chemical equilibrium. *P. Duden. Ber. chem. Ges. Berlin*, 33, *483* (*1900*). —The sodium salts of the benzolsulfamid of the heptyl and camphyl-amins are hydrolyzed to a great extent in water. The sodium salts themselves are but slightly soluble in alkaline solutions.

If benzol sulfocamphylamid is suspended in a ten percent solution of sodium hydroxid the oily sulfamid changes to the insoluble sodium salt. If ether be added to the solution the sodium salt disappears, and the sulfamid is found in the ether. Hence the ether acts as would an acid in decomposing the sodium salt. The process is explained as follows:

The sulfamid dissolves in the alkali, forming the sodium salt. This is insoluble in the alkali, and one gets a shifting of the equilibrium with the formation of more salt. If ether be present, the hydrolytically decomposed salt has the sulfamid removed by the solvent, and one gets a reverse change occurring till all the salt is decomposed.

With a 20 percent alkaline solution the hydrolysis is not great and the solution of the sodium salt occupies much more time. *C. G. L. W.*

Some double halids of cadmium with the methylamines and tetramethylammonium. *C. D. Ragland. Am. Chem. Jour.* 22, *417* (*1899*). —The author draws the conclusions:

"All the double halids of the alkali metals and ammonium with cadmium, described in the literature, may be classified under the types 1 : 1, 2 : 1, 3 : 1, 4 : 1.

"Among the double halids described in this paper, the types met with are 1 : 1, 2 : 1, 3 : 2, 1 : 2, 1 : 4.

"No double halids corresponding to the $(NH_4)_4CdCl_6$ and $(NH_4)_4CdBr_6$, i. e., the 4 : 1 type, were obtained.

"Of the twenty-one compounds described in this paper, eighteen conform to Remsen's law. Three fall under the extension of this law." *W. D. B.*

Some double halids of tin with the aliphatic amines and with tetramethylammonium. *C. G. Cook. Am. Chem. Jour.* 22, *434* (*1899*). —"A marked regularity is found throughout this whole series of salts. All of them, with one exception, belong to the 1 : 1 or 2 : 1 form, and all obey Remsen's laws as first stated." *W. D. B.*

Notes on the double halids of tin with the organic bases. *G. M. Richardson and M. Adams. Am. Chem. Jour.* 22, *446* (*1899*). —The authors have prepared and described a few compounds not made by Slagle (3, 508). *W. D. B.*

The double halids of antimony with aniline and the toluidines. *H. H.*

Higbee. Am. Chem. Jour. 23, *150* (*1900*). — Some 136 compounds were prepared and analyzed. *W. D. B.*

The precipitation of copper by zinc. *J. C. Shengle and E. F. Smith. Jour. Am. Chem. Soc.* 21, *932* (*1899*). — The authors find that when silver is precipitated by cadmium, or copper by either cadmium or zinc, the precipitated metal is always contaminated by the presence of the precipitating metal, zinc or cadmium, as the case may be. In two experiments with copper, over one percent of zinc was found while the amount ran up to about four percent in a third experiment. *W. D. B.*

Dissociation in the alkyl esters of nitric acid, sulphuric acid in the halogen acids. *J. U. Nef. Liebig's Ann.* 309, *126* (*1899*). — Monohydric alcohols can lose water in two ways, forming in the first instance ethylene and in the second ethylidene, CH_3.CH. The esters of the mineral acids may behave in the same way and the author shows that definite conditions favor the one or the other of these processes.

The reactions investigated were the action of alcoholic potash and sodium ethylate on the alkyl halids, the action of salts of silver with alkyl halids, the reaction of alkyl halids with amins, sodium malonic esters, and substances of this class, the reactions of the alkyl halids which do not form ethylene or methylene compounds by losing a halogen acid, the reaction of alkyl halids with sodium ethylate in the presence of freshly precipitated mercuric oxid, and the dissociation of alkyl nitrate and sulfate.

The formation of ethers from the reaction of alkyl halids with alkalies is due to the action of the alcohol on the alkylidene radicle. The formation of ethers by the reaction of silver salts with alkyl halid is explained similarly. Triphenyl methane forms halid derivatives which lose the halogen acid by heating. The compound formed in this reaction was not isolated. Diphenylene phenyl methane and triphenyl methane were formed.

The alkyl esters of nitric and sulfuric acid act as do the halogen derivatives. In all these cases, a certain amount of ethylene dissociation takes place. The presence of mercuric oxid has a marked effect on the action of sodium alcoholate on the lower alkyl halids. Neither the formation of esters nor olefines take place. The substances formed are similar to the mercarbid compounds investigated by K. A. Hofmann. With ethyl bromide the oxymercarbid nitrate is formed. The reactions were followed out in a quantitative manner as far as possible. *C. G. L. W.*

On the nitration of benzoic acid and of its methyl and ethyl esters. *A. F. Holleman. Zeit. phys. Chem.* 31, *79* (*1899*).—At -30°, 0°, and + 30°, the chief product is the metanitro compound, while relatively small amounts of the paranitro compound are formed. With rising temperature the relative yield of orthonitro and paranitro compounds increases, this increase being much more rapid with the esters than with the free acid. The analyses were made by titrating weighed portions of the solutions after they had been saturated with each one of the acids in turn. The results were then compared with known standards. This method gave an accuracy of about one percent. *W. D. B.*

The action of chromic acid on hydrogen. *C. L. Reese. Am. Chem. Jour.* 22, *158* (*1899*). — Chromic acid does not react with hydrogen at ordinary temperatures except in presence of platinum, asbestos, or of porous matter. At higher temperatures a reaction takes place. Electrolytic hydrogen does not reduce pure chromic acid in aqueous solution, but reduction does take place if sulfuric acid be present, the extent of the reduction varying with the concentration of the sulfuric acid.
W. D. B.

A new method for determining nitrates. *C. M. van Deventer. Zeit. phys. Chem.* 31, *50* (*1899*). — In the ordinary quantitative test for nitrates with sulfuric acid and ferrous sulfate, the brown color disappears when the solution is shaken and there is an evolution of gas. The author shows that the brown color does not disappear when ferrous sulfate is present in excess. On this he bases a titrimetric method. To prevent the mercury in the bottom of the burette from being attacked by sulfuric acid in presence of nitric acid, he adds a few cubic centimeters of bromoform. The ferrous sulfate solution must be added to the solution of nitrate and sulfuric acid, as the color change does not take place if a nitrate solution be added to a mixture of ferrous sulfate and sulfuric acid.
W. D. B.

Osmotic Pressure and Diffusion

The osmotic pressure of concentrated solutions. *T. Ewan. Zeit. phys. Chem.* 31, *22* (*1899*). — The author deduces a formula for the relation between osmotic work, change of freezing-point, and change of concentration when the heat of dilution is not neglected. From experiments on sugar and water, he works out an empirical relation for the change of osmotic pressure with the temperature at constant volume. This is a very interesting attempt, but the reviewer would have been pleased to have found a discussion as the effect of the heat of dilution on the relation between concentration and vapor-pressure at constant temperature. It would then be profitable to show whether and how the uncertainty in regard to the unit drops out when considering a reversible cycle.
W. D. B.

On the theory of diffusion. *Emil Bose. Zeit. phys. Chem.* 29, *658* (*1899*). — Mathematical expressions for the rate of diffusion in case of aqueous solutions of partially dissociated binary electrolytes are deduced by using the equation for the diffusion of a non-electrolyte, Nernst's equation for the diffusion of a complete dissociated electrolyte, and the equation of equilibrium. No experimental verifications are given. The author hopes that some one else will attempt to verify his formulas experimentally.
L. K.

Velocities

On inorganic ferments. *G. Bredig and R. Müller v. Berneck. Zeit. phys. Chem.* 31, *258* (*1899*). — The authors first point out the very striking analogy between the action of platinum black and that of organic ferments. They then study the effect of colloid platinum on the decomposition of hydrogen peroxid. The accelerating effect is still noticeable when the platinum concentration is one seventy-millionth normal. In neutral and acid solutions, the decomposition of H_2O_2 is a monomolecular reaction running to an end. The influence of the platinum concentration can be expressed by an exponential formula. In alkaline solution H_2O_2 behaves like a weak acid. Increasing the concentration of alkali first increases and then decreases the reaction velocity. The catalytic action of colloidal platinum is checked by H_2S, CS_2, HCN, $HgCl_2$, just as in the case of organic ferments. Experiments showed that colloidal platinum and quartz powder filled with air behave entirely differently with regard to different reactions. The article closes with a critical sketch of the different hypotheses advanced to explain catalytic action. *W. D. B.*

On the influence of catalytic agents on the oxidation of oxalic acid solutions. *W. P. Jorissen and L. T. Reicher. Zeit. phys. Chem.* 31, *142* (*1899*). — After a discussion of the historical development of the subject, the authors describe their own experiments, from which they draw the following conclusions:

In diffused light, the oxidation of oxalic acid solutions is accelerated by sulfuric and boric acids, the sulfates of manganese, iron, chromium, thorium, and erbium, cerous and ceric sulfates, sodium fluorid, and manganese acetate, butyrate, benzoate, and oxalate, while the sulfates of potassium, magnesium, and yttrium have no appreciable effect. In sunlight an acceleration was observed with the salts of manganese. The acceleration increases with the concentration of the catalytic agent. *W. D. B.*

The velocity of diazotization. *M. Schümann. Ber. chem. Ges. Berlin*, 33, *527* (*1900*). — Schümann has examined the reaction velocity of the system $R.NH_3Cl + HNO_2 = RN_2Cl + 2H_2O$. The reaction had been previously investigated by the author by colorimetric methods. In this investigation the change in the conductivity was used as a means of determining the reaction velocity. The reaction is a bimolecular one. He confirms his previous statement that all the aromatic amins diazotize with equal velocity. In the course of the work the molecular conductivities of sodium nitrite and nitrous acid were determined. For $NaNO_2$ at 25° $\mu_{32} = 102.0$; $\mu_{256} = 109.6$; $\mu_{1024} = 113.0$; $\mu_{\infty} = 115.5$; For HNO_2 at 25° $\mu_{512} = 150.1$; $\mu_{1024} = 187.5$; $\mu_{\infty} = 391.5$. The determinations of nitrous acid were made with sodium nitrite and hydrochloric acid. Control measurements with $AgNO_2 + HCl = AgCl + HNO_2$ were unsuccessful, as the reaction took place slowly and oxidation complicated the measurements. *C. G. L. W.*

On reaction velocities. *A. de Hemptinne. Zeit. phys. Chem.* 31, *35* (*1899*). — The author has determined the rate of catalysis of methyl acetate in various mixtures of water and acetone, and of water and glycerol. Curiously enough, the author seems to forget that the decomposition of methyl acetate is theoretically a bimolecular reaction, and that when we apply the formula for a monomolecular reaction the concentration of the water is hidden in the reaction velocity constant. Consequently, diluting the solution one-half would decrease the reaction velocity one-half if no other change took place. The reaction velocity constants are little, but not much, higher than they should be in case the acetone were considered merely as diluting the water and the acid. In the glycerol solutions, no satisfactory constant was obtained, one source of error apparently being the action of acetic acid on glycerol under the conditions of the experiment. *W. D. B.*

Reaction velocity in heterogeneous systems. *H. Goldschmidt. Zeit. phys. Chem.* 31, *235* (*1899*). — The author first takes up the catalysis of ethyl acetate in a mixture of benzene and water, the concentration of the ethyl acetate in water being calculable from the distribution ratio. It was found that the formula thus deduced did not describe the facts accurately because the reaction does not run to an end. In the benzene solution, the water is present in relatively small amounts, and therefore some ethyl acetate remains unacted upon. [This does not sound plausible. It is more probable that the important fact is the presence of the alcohol and the acetic acid in the benzene phase.] A new formula was deduced in which the distribution constants of alcohol and acetic acid were introduced. To determine the distribution coefficient of alcohol in benzene and water, a half-normal solution of alcohol and water was shaken with an equal volume of benzene at 25°, the water layer pipetted off and the concentration calculated from a freezing-point measurement. [No reference is made to the clouding of the solution as it was cooled, and we are not told what correction was made for the effect of the benzene on the freezing-point.] Experiments were also made on saponification of ethyl acetate in a mixture of benzene and water. While this is in many respects a very interesting and instructive paper, it is seriously marred by the disregard for facts. *W. D. B.*

The rate of action of water on certain α-, β- and γ-halogen substituted fatty acids. *E. de Barr. Am. Chem. Jour.* 22, *333* (*1899*). — Experiments were made at 150° as to the rate at which the halogen substituted acids are decomposed by water. The data are not worked up to test the reaction velocity formulas; but are used as a measure of stability. *W. D. B.*

On the velocity of reaction before complete equilibrium and before the transition point. *The real meaning of the law of chemical equilibrium of heterogeneous systems. The law of chemical reaction velocity in heterogeneous systems, etc. Meyer Wildermann. Zeit. phys. Chem.* 30, *341* (*1899*). — The article contains an account of some experiments on the velocity of crystallization of supersaturated solutions and allied phenomena, together with a good deal of abstract discussion under the above and other headings, which does not lend itself to condensation. *A. P. S.*

Electromotive Forces

Electromotive force and chemical equilibrium. *V. Rothmund. Zeit. phys. Chem.* 31, *69* (*1899*). — The author shows how the dissociation of a metallic oxid can be calculated from the electromotive force of the cell, Pt_0 | KOH | Oxid | metal. Attempts to confirm the formula experimentally with silver oxid and mercurous oxid failed because no satisfactory electrical measurements could be obtained with the silver oxid while the value for mercurous oxid extrapolated from data at 440° and 620° did not coincide with that obtained from the electrical measurements. The relation between the dissociation of hydriodic acid gas and the electrolytic dissociation of hydriodic acid in aqueous solution is also formulated. *W. D. B.*

Magnetic susceptibility of inorganic compounds. *S. Meyer. Wied. Ann.* 69, *236* (*1899*). — This paper contains a tremendous amount of detail in the way of reproducing observations on almost every inorganic compound. The conclusions from the work are that, as a rule, dia- or para-magnetic elements form dia- or para-magnetic compounds, that these properties are additive and that strongly magnetic compounds give results independent of the field strength within fairly wide limits. The author concludes the paper by giving a series of curves showing the relation of the magnetic susceptibility to the atomic volume.

H. T. B.

Electrolysis and Electrolytic Dissociation

The electrochemical equivalent of copper and silver. *T. W. Richards, E. Collins and G. W. Heimrod. Proc. Am. Acad.* 35, *123* (*1899*); *Zeit. phys. Chem.* 32, *301* (*1900*). — The present work was undertaken to reconcile the discrepancy in the values obtained for the atomic weight of copper deduced by purely chemical means and obtained by a comparison of its electrochemical equivalent with that of silver as determined by the ordinary form of silver voltameter. Whereas by the first method the atomic weight of copper is 63.604, by the second method, assuming Lord Rayleigh's value of the silver equivalent, it is about one part in one thousand smaller. The discovery of this apparent error in the silver voltameter led the authors to study both the copper and silver voltameters from the chemist's point of view.

The first part of the paper is devoted to the copper deposit, wherein it is shown that a greatest and least limit may be fixed, depending on the state of the solution, and that the effect of the size of the cathode is completely determinate provided the current density does not reach so high a value as to cause the deposition of hydrogen. The second part of the paper is devoted to the silver deposit, and a modified voltameter is devised, introducing a small porous pot to protect the anode, and a siphon to keep the solution always diffusing inwards away from the platinum cathode. Such a form when kept at a constant temperature (20° C) is shown to give exceedingly consistent results. Comparisons were made with other forms of voltameters, and as a result the porous cup voltameter was found to give a silver equivalent about 0.08 percent lower than that found by Rayleigh, Kohlrausch, and Kahle, and about 0.20 percent lower than the value given by the form of voltameter used by Patterson and Guthe. The effect of this lowering of the silver equivalent, instead of increasing it, as physicists have expected, is discussed briefly by the authors, but until the "porous cup" voltameter can be standardized no definite conclusions can be given.

H. T. B.

The ions of dilute sulfuric acid. *W. Starck. Zeit. phys. Chem.* 29, *385* (*1899*). — Sulfuric acid of various concentrations and of different temperatures was electrolyzed between platinum electrodes in cells patterned after those used by Hittorf and by Wiedemann. The changes in concentration around the electrodes were determined by titration and the transference numbers (*n*) for SO_4 were then calculated. With increasing concentration *n* increases. A five percent solution gave a lower value of *n* when electrolyzed in an apparatus containing a membrane of parchment or porous plate than when no membrane was interposed. This result is the opposite of that which Bein (4, 62) found for animal membranes, etc. According to Bein *n* increases with the temperature according to the equation $n = n_v[1 + a(\tau - \theta)]$, a being about 1/100 for 0.24 pct solution. The author finds that the expression holds also for higher concentrations (40 to 70 pct) and that a has about the same value

The author considers that at high concentration H_2SO_4 dissociates mainly into $\overset{+}{H}$ and $\overline{HSO_4}$, and at low concentrations into $\overset{+}{H}$, $\overset{+}{H}$, $\overset{=}{SO_4}$; which accounts for the decrease of n as the solution becomes more dilute. The increase of n with the temperature is attributed to the decrease in the frictional resistance encountered by the ions as the temperature rises, which factor must be greater than the change in conductivity due to the decrease of the number of $\overline{HSO_4}$ ions with rising temperature. [There are, however, no experimental facts upon which to base the latter statement.] *L. K.*

On ionic velocities. *O. Masson. Zeit. phys. Chem.* 29, *501* (*1899*). — Ionic velocities are measured directly by a method resembling in some respects that used by Lodge. The solution (colorless) to be tested is mixed with gelatin and placed in a tube of small bore. This tube is graduated and is completely filled with a gelatin salt mixture. The tube forms the connection between two flasks, its ends passing into side openings with which the flasks are provided. In one of the flasks is placed a solution of a salt with a colored cation, and a suitable electrode (copper sulfate solution and copper), while the other flask contains a solution of a salt with a colored anion together with another suitable electrode (sodium chromate solution and platinum). The current is passed from the former electrode to the latter and thus the contents of the tube gradually change color as the blue anions and the yellow CrO_4 ions move toward each other. The lines of demarcation between the colorless middle portion of the tubes and the colored portions at the ends are quite sharp and distinct. The ratio of the length of the blue portion of the tube to that of the yellow gives the ratio of the velocities of the cation and anion in the colorless solutions in the tube, since an advance of the colorless ions is accompanied by a relatively equal advance of the colored ions. Of course, this is based on the assumption that the rate of the movement of the colored ions is determined by that of the colorless ions in front of them. It is essential, too, that the colored ions, be of such character that they move more slowly than the colorless ones.

The migration numbers for the anions Cl and $\frac{1}{2}SO_4$ are smaller than those obtained by Hittorf and by Kuschel who, however, worked with more dilute solutions. The salts investigated are the chlorids of NH_4, K, Na, Li, and the sulfates of K, Na, Li, Mg. The author's results agree fairly well with those calculated by Kohlrausch for his conductivity determinations. The absolute velocities in the gelatin solutions are of course somewhat smaller than in the aqueous solutions. *L. K.*

Electrolytic determination of zinc in the presence of manganese. *E. J. Riederer. Jour. Am. Chem. Soc.* 21, *789* (*1899*). — Zinc can be separated from manganese by electrolysis if lactic acid, ammonium lactate, and ammonium bisulfate be added. The original solution should contain neither chlorids nor nitrates. The best current density is about 0.0025 amp/qcm and the solution should be kept stirred. *W. D. B.*

Electrolytic determinations and separations. *L. G. Kollock. Jour. Am. Chem. Soc.* 21, *911* (*1899*).—Data are given for the electrolytic separation of silver from platinum, copper, cadmium, zinc, nickel, cobalt, or iron; for the separation of mercury from copper, cobalt, nickel, zinc, cadmium, platinum, or iron; for the separation of gold from palladium, copper, nickel, cobalt, zinc, or platinum; and for the electrolytic precipitation of silver, cadmium, mercury, copper, iron, or bismuth from one or more solutions. *W. D. B.*

The electrolysis of metallic phosphate solutions. *H. M. Fernberger and E. F. Smith. Jour. Am. Chem. Soc.* 21, *1001* (*1899*).—The necessary data are given to show that after addition of disodium phosphate to the solution, copper can be readily and satisfactorily separated electrolytically from iron, aluminum, chromium, cobalt, zinc, nickel, or manganese. Copper can also be separated from solutions containing iron, cobalt, and zinc simultaneously. While nickel can be precipitated readily and satisfactorily from a solution to which disodium phosphate has been added, a separation from manganese or chromium proved impossible, as the precipitated nickel then contained phosphorus. Mercury precipitates nicely and can be separated from zinc. Many difficulties were encountered in trying to separate copper or mercury from uranium, and this point is to be the subject of further investigation. *W. D. B.*

An electrolytic study of benzoin and benzil. *J. H. James. Jour. Am. Chem. Soc.* 21, *889* (*1899*).—The electrolytic oxidation of benzoin in sodium hydroxid solution with an anode density of 0.0025 amp/cm^2 gave a maximum yield of benzoic acid (18 percent), while higher densities gave less acid and larger quantities of tarry decomposition products. With sulfuric acid solution, a current density of 0.05 amp/cm^2 was necessary to effect oxidation, while a further increase in current density gave less acid and more tarry products. In hydrochloric acid solution with a current density of 0.01 amp/cm^2 both benzoic acid and benzil are obtained; with higher densities, less acid, more benzil and more tar. The electrolytic reduction of benzoin in acid solutions gave small quantities of a substance melting at 205°–206°. The electrolytic reduction of benzil gave chiefly benzoin in acid solutions, while the results were unsatisfactory in alkaline solutions. A 14.5 percent yield of benzoic acid was obtained by electrolytic oxidation in sulfuric acid solution and practically nothing in hydrochloric acid or alkaline solutions. Attempts to oxidize toluene were not successful. *W. D. B.*

The electrolytic oxidation of succinic acid. *C. H. Clarke and E. F. Smith. Jour. Am. Chem. Soc.* 21, *967* (*1899*).—In most of the experiments, the solution at the anode consisted of sodium succinate and an excess of sodium hydroxid dissolved in aqueous alcohol. It was shown by the electrolytic oxidation of succinic acid there are formed tartaric acid, oxalic acid, some aromatic bodies, oxygen, carbon monoxid, carbon dioxid, ethylene and methane. The authors did not succeed in stopping the reaction either at the tartaric acid or the oxalic acid stage. *W. D. B.*

The persulphates of rubidium, cesium and thallium. *A. R. Foster and E. F. Smith. Jour. Am. Chem. Soc.* 21, *934* (*1899*).—The authors give data for the electrolytic preparation of the persulfates of rubidium, cesium and thallium. They recommend a current density at the anode of 0.2–0.3 amp/cm^2. Thallium persulfate is so instable that it could not be isolated for analysis.

W. D. B.

The cause of the change in conductivity of lead peroxid. *T. Sundorph. Wied. Ann.* 69, *319* (*1899*). — The effect of the increase in resistance produced by the continuous passage of an electric current through PbO_2 is shown by the author to be probably due to the formation of a badly conducting layer over the metal electrodes in the powder. The action of electric waves on the powder in producing a similar conversion of PbO_2 into PbO in the neighborhood of the electrodes is due to the small sparks induced, and is shown by an analysis of the lead powder in the interior and near the sides.

H. T. B.

The specific gravity and electrical resistance of metallic tellurium. *V. Lenher and J. L. R. Morgan. Jour. Am. Chem. Soc.* 22, *28* (*1900*). — The specific gravity of tellurium at 20° was found to be 6.199, but this is probably a trifle too low. Values for the specific resistance vary from 280 to 1100, variations in contact and structure having an enormous effect. The authors look upon the lowest values as probably the best.

W. D. B.

A new method for determining inversion temperatures. *E. Cohen. Zeit. phys. Chem.* 31, *164* (*1899*). — The author measures the resistance of saturated solutions and plots these values against the temperature. If there is a change in the nature of the substance with respect to which the solution is saturated, this will cause a break in the curve at that temperature. In the case of hydrated zinc sulfate, the inversion temperature was found to be 39.0° by this method, as against 38.50° by the dilatometer and 38.75° by the inversion cell. The author next takes up the question of internal resistance of the Daniell cell when the copper sulfate solution is saturated and the zinc sulfate solution is not. Copper sulfate with five of water ceases to be solid phase at about 56° and this fact shows itself in the curve for the internal resistance of the Daniell cell. The author calls attention to the fact that the smooth curve obtained by Carhart is due to the leaving out of the observation at 56°.

W. D. B.

The influence of the substituents on the electrical conductivity of benzoic acid. *A. Tingle. Jour. Am. Chem. Soc.* 21, *792* (*1899*). — The conductivity of two dilutions has been determined for several salts of a number of substituted benzoic acids. The difference between the sodium and potassium salts of the same acid was not constant and no conclusions were drawn.

W. D. B.

Three additions to the Kohlrausch-Ostwald conductivity method. *J. L. R. Morgan. Jour. Am. Chem. Soc.* 22, *1*, *23* (*1900*). — In order to get a clear high note in the telephone, the author suggests a modified form of Pupin's electrodynamic interrupter. It is also suggested that spools be kept in stock giving multiples of the bridge wire, these to be inserted in series so as to make the reading come in the middle of the bridge. [There seems to be a misunderstanding here. The reading in the middle of the bridge is more accurate than at the end, only because it is the ratio of the two arms, which enters into the formula. If the reviewer has understood the arrangement, this is not the case in Mr.

Morgan's apparatus. What has been accomplished is that an error in reading of one millimeter makes less of an error on a long bridge than on a short one.] In order to avoid the uncertainty whether two successive readings on either side of the mean give the same tone, the author has two sliding contacts and takes the mean of the positions at which the two give the same tone. This is a very ingenious arrangement, and would appear to be a real improvement. *W. D. B.*

Dissociation equilibrium of strong electrolytes. *H. Euler. Zeit. phys. Chem.* 29, *603* (*1899*). — The author wrestles with the old question as to why aqueous solutions of strong electrolytes do not follow Ostwald's dilution formula. After considering Noyes's views that $\frac{\lambda v}{\lambda \infty}$ does not accurately express the degree of electrolytic dissociation, Arrhenius's opinion that the law of mass action does not apply in the usual form to these cases, and Jahn's idea that ionic velocities are not constant at all dilutions, he arrives at the conclusion that the derivation from Ostwald's formula is very likely due to a change which the salt causes in the dissociating power of the solvent. That the real difficulty lies in the fact that the theory of electrolytic dissociation is inadequate does not seem to have occurred to the author. *L. K.*

The dilution law. *W. D. Bancroft. Zeit. phys. Chem.* 31, *188* (*1899*). — There being no known radical distinction between strong and weak electrolytes, the author revives Storch's suggestion of a dilution law with an exponent, varying from one electrolyte to another, the Ostwald and the van 't Hoff formulas being special cases under the general head. The great difficulty in testing this or any other hypothesis is that the migration velocities do change with the concentrations, and we have therefore no means at present of determining the dissociation accurately. The point might also have been made that no formula of this type will serve for cases like acetic acid and water where we can pass continuously from one hundred percent of one to one hundred percent of the other. *W. D. B.*

The change in the strength of the weak acids on addition of salts. *S. Arrhenius. Zeit. phys. Chem.* 31, *197* (*1899*). — The author has attempted to show, from experiments on the inversion of sugar, that salts increase the dissociation of weak acids. The corrections to be applied to the results are large, because the neutral salts have an effect on the rate of inversion any way, and because there may be double decomposition with the acid. After making these corrections, the author concludes that the addition of salts does increase the apparent dissociation according to an exponential formula. It is next pointed out that if we mix equimolecular solutions of ammonium chlorid and potassium chlorid, the dissociation must be forced back in case the salts follow the van 't Hoff dilution law. This is said not to be the case experimentally, and the author reiterates his belief that the concentration of the ions is the only important matter and that the concentration of the undissociated substances is not a factor. This would seem to play havoc with most of our general equilibrium theory. The author draws this conclusion and states that, on adding potassium chlorid to a thallium chlorid solution, the total amount of thallium chlorid in solution can be forced below the amount of undissociated thallium chlorid in water alone. If this be true, we can no longer postulate that the concentration of the undissociated portion of the salt remains constant. Arrhenius states his belief that the solubility of the undissociated salt is affected by the addition of everything which is certainly true as regards alcohol. It almost seems possible that the time may be coming when facts will not be ignored because they do not conform to the theory, and when it will be recognized that one loses more than one gains by working with such dilute solutions that the difference between all possible hypotheses falls within the limit of experimental error.

W. D. B.

Contribution to the study of aqueous solutions of double salts. *H. C. Jones and N. Knight. Am. Chem. Jour.* 22, *110* (*1899*). — Conductivity measurements on a number of double bromids and chlorids showed that the variations from the sum of the conductivities of the single salts are greater than in the case of mixtures which do not form double salts. Under this latter head come potassium and ammonium chlorid. When equivalent quantities of these two salts are mixed, the percentage decrease from the sum is about thirteen percent when the initial solutions are normal and a little over two percent when they are eightieth normal. *W. D. B.*

Physico-chemical investigations of uranyl salts. *C. Dittrich. Zeit. phys. Chem.* 29, *449* (*1899*). — Aqueous solutions of uranyl salts of inorganic and organic acids were investigated by means of cryoscopic and conductivity methods. All results are interpreted in terms of the dissociation theory. The rapid increase of the molecular conductivity with the dilution indicates that the salts are hydrolytically decomposed. The cryoscopic determinations indicate that the nitrate and chlorid are highly dissociated, the sulfate, acetate, and tartrate on the other hand only slightly. The migration number of $\frac{1}{2}UO_2$ was found to be 56 at 25° C. The molecular conductivity of uranyl salts increases with the affinity constant of the acids. Complex ions are formed when solutions of sodium salts of fatty acids are mixed with solutions of uranyl salts, as indicated by the freezing-point determinations, calorimetric measurements, and a qualitative inspection of the changes that occur at the electrode, upon electrolyzing the solution. This means that the sodium salts of the complex uranyl acetic, — oxalic, tartaric, citric, etc. — acids are formed under the above named conditions. The author assigns to the complex sodium uranyl oxalate the formula $Na\,UO_2(C_2O_4)_2$. When uranyl nitrate is mixed with sodium salts of organic acids heat is absorbed, except in the case of sodium oxalate. A solution of the latter salt when mixed with uranyl nitrate solution results in evolution of heat.

L. K.

On the action of very dilute nitric acid. *A. van Bijlert. Zeit. phys. Chem.* 31, *103* (*1899*). — The author cites a number of very interesting experiments in support of the view that undissociated nitric acid is an oxidizing agent, while the dissociated acid in presence of a metal is a reducing agent, though the result is usually an auto-reduction. *W. D. B.*

Dielectricity and Optics

On the comparative efficiency as condensation nuclei of positively and negatively charged ions. *C. T. R. Wilson. Phil. Trans.* 123, *289* (*1899*). — Working in behalf of the Meteorological Council, the author studies the questions whether atmospheric air in the regions in which rain is formed is likely to contain free ions, and whether the positively and negatively charged ions differ in their efficiency as condensation nuclei. To show that the negative ion has a greater power of condensing water around it would be to show that by the effect of gravity alone an electrified atmosphere could be produced and negatively charged rain. The author's method of treatment is the already well known one of sudden expansion of air, producing supersaturation and fog. The presence of free ions in air is indicated by the fact that, in moist dust-free air, when allowed to expand suddenly, a slight rain-like condensation is produced, if the maximum supersaturation attained exceeds a certain limit. This limit being the same required to produce fogs in air ionized by Röntgen rays.

The results of the work show that a four-fold supersaturation, ($\frac{v_2}{v_1} = 1.25$), only is required to make water condense on negative ions, while for positive ions a six-fold, ($\frac{v_2}{v_1} = 1.31$), supersaturation is required. Hence if the condensation nuclei in the atmosphere are ions they must be restricted to the negative, and thus a negative charge will be carried down, by precipitation, to the earth's surface. The final consideration in regard to the presence of free ions in air, in the absence of ionizing agents, is that they cannot be regarded as free unless the process producing the supersaturation causes the ionization. *H. T. B.*

On the electric charge in electrolytic gas. *W. Kosters. Wied. Ann.* 69, *12* (*1899*). — The author endeavors to show that the electric charges found by Townsend in various gases formed by electrolysis are identical with the phenomenon described by Lenard of the charge provided by dropping water.

H. T. B.

On the activity of oxypyrotartaric acid. *J. H. Aberson. Zeit. phys. Chem.* 37, *17* (*1899*). — Oxypyrotartaric acid was considered by Will to be a ketone acid and to be optically active. As under these circumstances there is no asymmetric carbon, the van 't Hoff-Le Bel theory enables us to predict that one of these conclusions must be wrong. The author shows that it is the second which is faulty, the optical activity being due to traces of impurity.

W. D. B.

On the refractive indices and densities of normal and semi-normal aqueous solutions of hydrogen chlorid and the chlorids of the alkalis. *J. Conroy. Proc. Roy. Soc.* 64, *308* (*1899*). — Great pains were taken with the measurements of the physical properties, but commercial chemicals were used. *W. D. B.*

On the refractive indices of metals. *E. van Aubel. Zeit. phys. Chem.* 39, *565* (*1899*). — Calculation of the refractive index of metals based on the refraction of the solutions of their salts lead to numbers differing widely from the direct determination of the same constant by Drude. *F. B. K.*

The rôle of the medium in solution. *J. W. Brühl. Zeit. phys. Chem.* 30, *1* (*1899*). — This paper contains an account of an attempt to get at the influence of the solvent upon the properties of the solute, from a new standpoint, — that of tautomeric changes. The materials employed were the methyl and ethyl esters of α-mesityloxid oxalic acid, which pass reversibly from the enol form $R_2C = CR - OH$, to the keto form $R_2CH - CR = O$. A very great difference in the refractive and dispersive power of the two forms makes these two substances particularly valuable for such study, by rendering it quite easy to trace the course of the transformation by optical means. On studying the action of various solvents, Brühl finds that these may be divided into three groups: (1) chloroform in which the transformation from enol to keto form does not go on at all, at ordinary temperatures; (2) benzene, carbon disulphide, brom-naphthalene, in which the change goes on, though slowly; (3) methyl and ethyl alcohol where it proceeds with relatively very great velocity. Hence the solvents which are most active in this respect, are those which possess the greatest ionizing power and the highest dielectricity constant.

Brühl then devotes a good deal of space to showing that a connection does also exist, at least a qualitative one, between the specific heat, heat of fusion, heat of vaporization, and what he calls the "medial" energy (energy of the medium in ionization, etc.).

His explanation of the manner in which the transformation in hand goes on, is that the enol form is dissociated into hydrogen as ion and a negatively charged residual ion; recombination then takes place in such a way as to produce the keto form, which is not susceptible of dissociation. Direct proof of such a dissociation of the enol form is, as yet, wanting. *A. P. S.*

On phototropism. *W. Marckwald. Zeit. phys. Chem.* 30, *140* (*1899*). — The term phototropism is applied to alteration in the properties of a substance produced by the action of light when the changes are of a temporary nature and disappear sooner or later after cessation of illumination. Two compounds are described, the anhydrous chlorid of a quinoquinolin and β-tetrachlor-keto-naphthalene, which exhibits remarkable temporary color changes under the influence of light.

F. B. K.

The color changes of illuminated substances. *H. Biltz. Zeit. phys. Chem.* 30, *527* (*1899*). — Attention is called to several cases of "phototropism."

F. B. K.

Note on the color of chlorine solutions. *E. H. Sarles. Jour. Am. Chem. Soc.* 21, *1038* (*1899*). — "On passing chlorine into ethyl alcohol to make chloral, the liquid finally separated into a lower yellow layer, and an upper green layer. The upper layer was a grass-green, not a yellowish-green." The cause of this green color has not yet been ascertained. In preparing the green solution, "the best results have so far been obtained by cooling the alcohol to about —15° with ice and crystallized calcium chloride while passing the chlorin in."

W. D. B.

Crystallography, Capillarity and Viscosity

Crystalline form of iodoform. *W. J. Pope. Jour. Chem. Soc.* 75, *46* (*1899*). — Iodoform crystallizes nicely from acetone. The crystals belong to the hexagonal system. *W. D. B.*

On the surface-tension of mercury. *G. Meyer Verh. phys. Ges. Berlin,* 17, *56* (*1898*). — Reviewed (3, 190) from Wied. Ann. 66, 525 (1898).

The least thickness of liquid films. *K. T. Fischer. Wied. Ann.* 68, *414* (*1899*). — The author shows and discusses the discrepancies in the work of previous observers and as a means of more easily realizing the true conditions for the production of oil films proposes the use of mercury surfaces instead of water. The purity of the mercury being of such importance, the method of purification is discussed at length. In all, 180 experiments were tried on rape seed oil, olive oil, glycerin water solutions, and dilute soap solutions. For these substances the thickness of an equal sized connected film is safely less than 5×10^{-6} mm.

H. T. B.

On the viscosity of solutions of certain esters in supercooled thymol. *C. Schall. Zeit. phys. Chem.* 29, *423* (*1899*). — The object of the investigation is to test Jäger's theory for viscous liquids. This theory is to the effect that the quantity of a substance which must be dissolved in a liquid in order to bring about a change in its viscosity equal to that due to a certain rise of temperature, causes a depression of the freezing-point equal to that rise. The method is therefore available for determining molecular freezing-point depressions.

In an earlier paper, glycerin was studied in this way. The esters used in the present investigation were amyl propionate, ethyl valerate, and ethyl acetate. Two series of results give values which fall well into line, while three others show a considerable variation, especially for determinations made at higher temperatures.

A. P. S.

The thermal deformation of the crystallized normal sulphates of potassium, rubidium and caesium. *A. E. Tutton. Proc. Roy. Soc.* 64, *350* (*1899*). — The thermal deformation constants of the crystals of the normal sulfates of potassium, rubidium, and caesium exhibit variations which, in common with the morphological, optical, and other physical properties previously investigated, follow the order of progression of the atomic weights of the alkali metals which the salts contain.

W. D. B.

On the partial association of liquid molecules. *J. J. van Laar. Zeit. phys. Chem.* 31, *1* (*1899*). — From the measurements of Ramsay and Shields, on the apparent dissociation of water, the author has calculated the heat of association from the van 't Hoff formula for the relation between the equilibrium constant and the temperature. The heat of association thus calculated is fairly independent of the temperature if we assume that the reaction can be expressed by the equation $(H_2O)_2 \rightleftarrows 2H_2O$. With ethyl alcohol satisfactory results are obtained by assuming the equation $(C_2H_5OH)_2 \rightleftarrows 2C_2H_5OH$. With methyl alcohol the chief reaction appears to be $(CH_3OH)_3 \rightleftarrows 3CH_3OH$, though something evidently occurs also.

The author refers the changes of volume when water and alcohol are mixed to the changes in dissociation of the two substances. Since the change of $(H_2O_2)_2$ into $2H_2O$ is accompanied by a decrease in volume, a rise of temperature would cause a contraction if no other factor need be taken into account. This phenomena will be more or less completely masked by the normal expansion due to the rise of temperature. In the case of water, the dissociation effect determines the sign of the change between 0° and 4°. The author points out that the irregular expansion of water can thus be accounted for with a certain degree of qualitative approximation.

W. D. B.

On the surface-tensions of mixtures of sulphuric acid and water, and the molecular mass of sulphuric acid. *C. E. Linebarger. Jour. Am Chem. Soc.* 22, *5* (*1900*). — Addition of water to sulfuric acid or of sulfuric acid to water increases the surface-tension. The surface-tension of concentrated sulfuric acid is practically independent of the temperature between 0° and 50°. The author calls attention to the fact that this indicates an enormous degree of polymerization, if we are to draw conclusions from the formula of Ramsay and Shields.

W. D. B.

Note on some properties of the radiation of uranium and other radio-active substances. *H. Becquerel. Comptes rendus*, 128, *771* (*1899*). — The intensity of the radiation of uranium, polonium, and radium, appears to undergo no perceptible change with time. There is no evidence of polarization in the uranium rays and the earlier statement of a direct reflection must now give way to one of diffuse reflection. Experiments on refraction gave contradictory results. The rays from polonium are much more readily absorbed than those from uranium or radium.

W. D. B.

On the action of light at low temperatures. *A. and L. Lumière. Comptes rendus*, 128, *359*, *549* (*1899*). — At the temperature of liquid air, photographic plates are only very slightly affected by light. The change is a reversible one, the sensitiveness returning with rising temperature. Phosphorescence also ceases at these low temperatures.

W. D. B.

On the phosphorescence of strontium sulfid prepared from strontium carbonate and sulfur vapor. *J. R. Mourelo. Comptes rendus*, 128, *427*, *557* (*1899*). — Strontium sulfid made from strontium carbonate and sulfur vapor is not crystalline and is phosphorescent only when the substance is made at a red heat or at a lower temperature and then raised to a red heat. A white heat destroys the phosphorescence. Diffused light is more effective in producing phosphorescence than sunlight. The author noticed also what he calls the phenomenon of auto-excitement.

W. D. B.

On the activity of manganese with reference to the phosphorescence of strontium sulfid. *J. R. Mourelo. Comptes rendus*, 128, *1239* (*1899*). — If a trace of the basic nitrate of bismuth or of the carbonate of manganese be added to strontium sulfid and the mass be heated to a red heat for three hours, the sulfid will phosphoresce with a clear green light when cooled. *W. D. B.*

Light phenomena produced by the action of certain ammoniacal salts on fused potassium nitrite. *D. Tommasi. Comptes rendus*, 128, *1107* (*1899*). — Light is evolved when a crystal of ammonium chlorid, sulfate, or nitrate is thrown into fused potassium nitrite.

W. D. B.

ON THE WESTON CELL AS A TRANSITION CELL AND AS A STANDARD OF ELECTROMOTIVE FORCE, WITH A DETERMINATION OF THE RATIO TO THE CLARK CELL

BY H. T. BARNES

Kohnstamm and Cohen[1] have recently made a careful study of the inversion point that occurs in the temperature curve of cadmium sulphate. They have shown conclusively by solubility determinations, by a transition cell of the second type and by the dilatometer, that this change takes place in the neighborhood of 15° C. Jaeger and Wachsmuth,[2] in their paper on the cadmium cell, noticed this change as an irregularity in their cells, but otherwise did not give it further consideration. As yet it appears, so far as the author is aware, that no experiments have been published where the discontinuity is shown by a change in the E. M. F. temperature curve of a Weston cell. No idea can be obtained from the experiments of Jaeger and Wachsmuth as to the position of this important transition point, on account of the method they used of determining the temperature change, but it is a matter of very little difficulty to employ the Weston cell as a transition cell of the fourth type, in a manner similar to the Clark cell.[3]

It is proposed in the present paper to describe some experiments on this point, which, although carried out before the paper was published by Kohnstamm and Cohen, stand in good accord with their results.

The primary object of the work was not so much to de-

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[1] Wied. Ann. 65, 344 (1898).

[2] Ibid. 59, 575 (1896).

[3] Jour. Phys. Chem. 4, 1 (1900).

termine the temperature change of the cell as to prepare a set of Weston cadmium standards for comparison with the Clark cells in the possession of the laboratory. However certain experiments led the author to study more in detail the cell itself. It was soon seen that the temperature change was somewhat in excess of the formula proposed by Jaeger and Wachsmuth, and although perfectly consistent and regular above 15° C. for the types of cells used, yet showed such large discrepancies below 15° as to leave no doubt that they were inherent in the cells themselves and could not be attributed to any possible error of experiment. The question naturally arose whether the discontinuity in the curve was similar to that in the Clark cell at 39° C., but it was seen that the break was by no means so sharply defined. The great viscosity of the cadmium sulphate solution when nearly saturated, and the extreme slowness with which the last quantity of salt is dissolved, renders it very probable that this would be so even if the break could be attributed to a change in hydration. From a careful examination of the salt above and below 15°, Kohnstamm and Cohen were led to the idea that a change in crystalline form occurred. This would be difficult to show, but seems to explain more conclusively the existing data.

Temperature change of the Weston cell given by previous observers

From the experiments of Dearlove[1] on the Weston cadmium cell the fact is very evident that the form of cell originally recommended by Weston and described in his patent specifications, was very irregular and uncertain. From the value 0.01 percent, as given by Weston for the temperature change per degree, Dearlove found values ranging to 0.003 percent. These he was unable to connect with properties of the cells, although he explained very well the cause for the irregularities between different cells. This uncertainty in the temperature coefficient was so marked that in concluding his remarks on the test of seven cells sent him by Dr. Muirhead, he says, "The temporary

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[1] Electrician, 31, 645 (1893).

coefficient of the above cells between 2.5° C. and 22° C. was found to be 0.008 percent."[1]

In the extensive experiments of Jaeger and Wachsmuth they do not attempt to explain the irregularities in the cells used by Dearlove, although they appear to have been aware of his results. Their experiments comprise comparisons of several cells set up in the H-form with different chemicals, and strengths of amalgam. They determine the temperature change of the E. M. F. by measuring the difference between six cells in paraffin baths at different temperatures, but do not attempt to carry the cells through a temperature cycle. They study the effect of impurities in the ingredients of the cell and show the portable nature of the cell by comparing with a standard before and after making a journey of 600 Km. The agreement between the calculated and observed values of the temperature change is most satisfactory, seldom exceeding 0.01 millivolt. At the same time, the range is not large, only in three instances being as much as 18°. Three experiments only were made as high as 26° and the greatest range at this limit was between a cell at 17.8° C. and one at 25.9° C. Most of the tests were made, however, below 18°. The temperature formula deduced from these tests reads in millivolts.

$$E_t = E_{20} - 0.038\,(t - 20°) - 0.00065\,(t - 20°)^2.$$

The authors, however, remark "Diese Formel gilt nach ihrer Ableitung zwischen 0° und 25°, doch haben spätere Beobachtungen gezeigt, dass einige Elemente sich zwischen 0° und etwa 5° in der Weise unregelmässig verhalten, dass ihre electromotorische Kraft bedeutend (etwa $\frac{1}{1000}$ V.) grösser ist, als diejenige der anderen Elemente. ... Der Bereich der obigen Formel ist daher vorläufig auf die Temperaturen zwischen 25° bis oberhalb 5° zu beschränken."[2] In a footnote given in the paper of Kohnstamm and Cohen, authorized by Prof. Jaeger, it appears that 5° should read 15°. In this case the remarkable

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[1] l. c. p. 647.

[2] loc. cit. p. 583.

agreement of the observations of Jaeger and Wachsmuch extending below 15° with their formula must be regarded as accidental. The temperature change per degree given by the above formula is almost exactly one-half of the value found by Dearlove and only about one-third of the value given by Weston.

Present experiments

The experiments about to be described were very much facilitated by the constant temperature water-baths and electrical and temperature measuring instruments employed in the author's study of the Clark cell. The method of carrying out the experiments was also the same. In constructing the Weston cell in test-tube form, the B. O. T. type of crystal cell was followed except that it was inverted. This is due to the necessity of using cadmium amalgam in place of a rod. This inverted cell has been already described in another place.[1]

The following list comprises a brief description of the cells used in the present work:

Cd_1

A cell prepared similar in every respect to a B. O. T. test-tube "crystal" Clark cell, except in the use of moist crystals of cadmium sulphate in place of zinc sulphate, and an amalgamated cadmium rod in place of a zinc rod. The cadmium was carefully tested and found free from any trace of zinc. The cadmium sulphate was chemically pure and found neutral. It was not recrystallized or treated with mercurous sulphate. The paste was prepared by mixing pure washed mercurous sulphate with moist cadmium sulphate crystals. The positive electrode was a flattened platinum wire, amalgamated.

Cd_2

Similar in every respect to Cd_1 except in the use of a cadmium rod not amalgamated.

$Cd_3Cd_4Cd_5$

Cells made in the inverted type with a cadmium amalgam

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[1] Electrician, 39, 68 (1897); 40, 165 (1897).

of 1 to 6 proportion, as recommended by Jaeger and Wachsmuth.

Cd_H

H-form of cell made after type III of Jager and Wachsmuth.

Cd_6 Cd_7

Cells of the inverted type with a 1 to 6 amalgam. These cells differed from the other inverted cells only in having cadmium sulphate treated with mercurous sulphate before recrystallization.

A comparison of these cells is given in Table I, and shows the divergence in millivolts from the mean.

TABLE I

Cell	Mar 11, 1897	Mar 18th	Mar 20th	Mar 22nd	Mar 27th
Cd_3	−0.04	−0.08	−0.07	+0.02	0
Cd_4	0	+0.01	+0.12	+0.11	+0.08
Cd_5	−0.02	+0.01	+0.02	+0.10	+0.14
Cd_6	....	+0.03	−0.32	−0.34	−0.32
Cd_7	....	−0.04	−0.04	+0.01	−0.08
Cd_H	+0.06	+0.09	+0.30	+0.28	+0.17

Cells Cd_1 and Cd_2, being made with cadmium stick, were much higher than the amalgam cells. Cd_1 was 6.46 millivolts higher than Cd_2 and no less than 44.0 millivolts higher than Cd_3. A complete test of the temperature change was made on three of the cells included in the table over the range 0° to 40°, between March 18th and 20th, which no doubt is the reason for the permanent change in the E. M. F. for Cd_6 and Cd_H. The agreement of all the cells before this test is a sufficient proof that the divergence noted in these two cells is not to be ascribed to the manner of construction.

TABLE II

Temperature coefficient Weston Cadmium cell

March 19, 1897

Temperature	Cd_4	Cd_8	Cd_H	Formula $-0.086\,(t-15^\circ)$
0° C	+2.07	+4.33	+3.64	....
1.5	1.64	3.68	3.08	....
2.9	1.26	3.30	2.59	....
3.8	0.99	3.02	2.33	....
5.0	0.69	2.64	1.93	....
7.3	0.21	1.90	0.86	....
9.6	0.14	1.17	0.32	....
11.8	0.23	0.55	0.17	....
13.8	0.07	0.11	0.02	....
15.0	0	0	0	0
18.6	−1.27	−0.22	−0.37	−0.31
20.1	0.49	0.36	0.58	0.44
24.2	0.83	0.73	1.00	0.79
29.3	1.16	1.20	1.38	1.23
27.1	0.87	1.11	0.98	1.04
32.6	Put at	1.57	1.66	1.51
38.1	15°	1.99	2.02	1.99
40.5	....	2.17	2.19	2.19
39.6	....	2.08	2.05	2.11
36.1	....	1.70	Put at	1.81
30.5	....	1.24	15°	1.33
25.7	....	0.92	....	0.92

The results of the experiments on the temperature change are contained in Table II and are plotted in Fig. 1. The formula of Jaeger and Wachsmuth (J. & W) is also shown for comparison. It appears that these cells follow within the limits of experimental error a linear formula

$$E_t = E_{15} - 0.086\,(t - 15^\circ),$$

which agrees almost exactly with the mean temperature change found by Dearlove. The continuity of the line alters at 15, under which limit no regularity can be said to exist except approximately in the slope. The tests given here were obtained by bringing the cells up by intervals from 0°, where they had remained over night, allowing ample time at each interval for the attainment of a steady and uniform temperature. The divergence in the cells at 0° is very large, amounting in the extreme to two millivolts, and persists for hours without showing any signs of change. The E. M. F. of the cells, however, converges when approaching 15°, and from that point to 40° it shows perfect regularity. The return from 40° was also along the same line.

TABLE III
Inversion of cadmium sulphate
March 22, 1897

Temp	Cd_6		Cd_5		Cd_4	Cd_H
15.0	0	unstable	0		0	0
14.2	+0.13		+0.08	unstable	+0.17	+0.19
12.0	+0.23		+0.27		+0.45	+0.53
10.1	+0.39		+0.46		+0.69	+0.84
8.2	+0.61		+0.66		+0.97	+1.05
5.2	+0.90		+0.78		+1.34	+1.62
2.0	+1.26		+0.95		+1.62	+2.04
2.0	+1.26		+1.70		+1.62	+2.04
0°	+2.19		+1.85		+1.89	+2.38

In Table III some tests are given which were made to see whether a sudden change in E. M. F. could be noticed on cooling a cadmium cell slowly from 15° to 0°. These results are represented in Fig. 2 and show the effect on cells Cd_5 and Cd_6. Cells Cd_4 and Cd_H do not show any sudden change at all. The two former cells follow the slope of the temperature curve above 15° until about 2°, when a sudden increase in E. M. F. takes place. In Fig. 1 on the ascending series (Cd_4), a somewhat similar effect is seen to occur between 8° and 15°. The unstable E. M. F. over this limited range, which is just about the mean temperature of the range of Jaeger and Wachsmuth's determinations, follows quite closely their temperature formula. It is evident that the point of actual crossing of the two branches of the curve must occur very nearly at 15° C. Various other tests were made to determine the temperature change above and

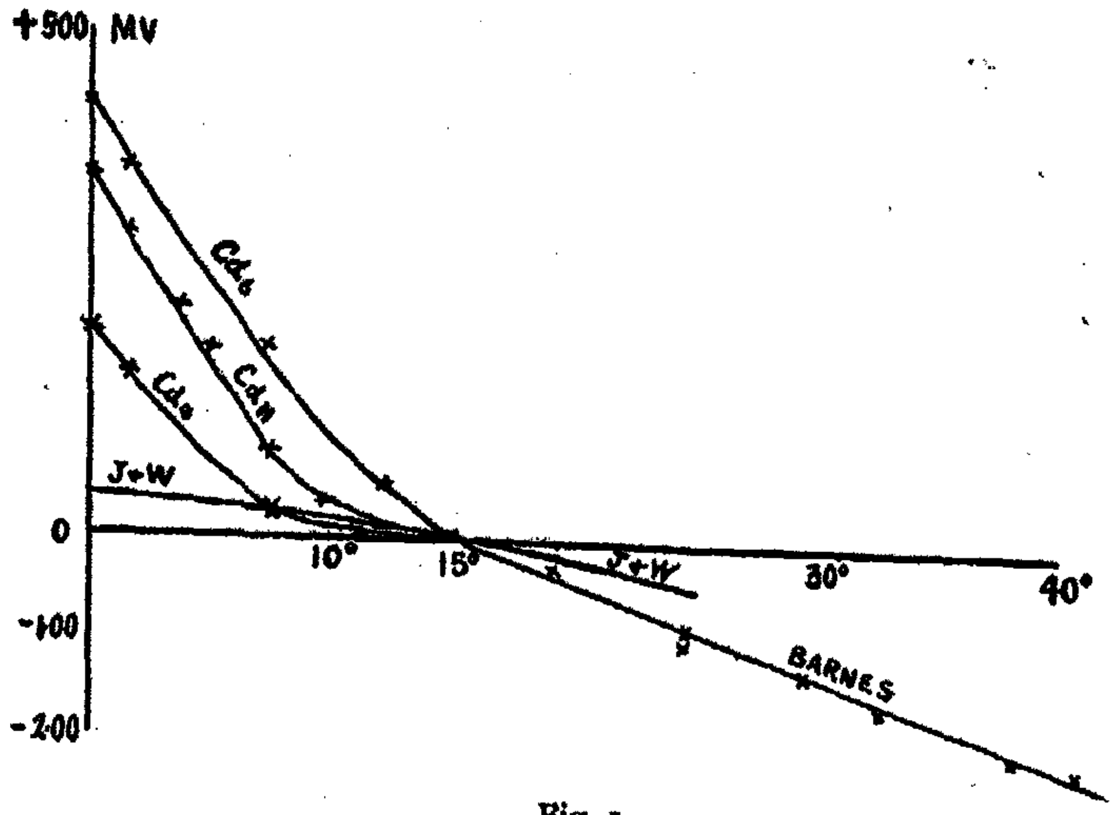

Fig. 1
Temperature coefficient cadmium cells. J. & W. Formula proposed by Jaeger and Wachsmuth

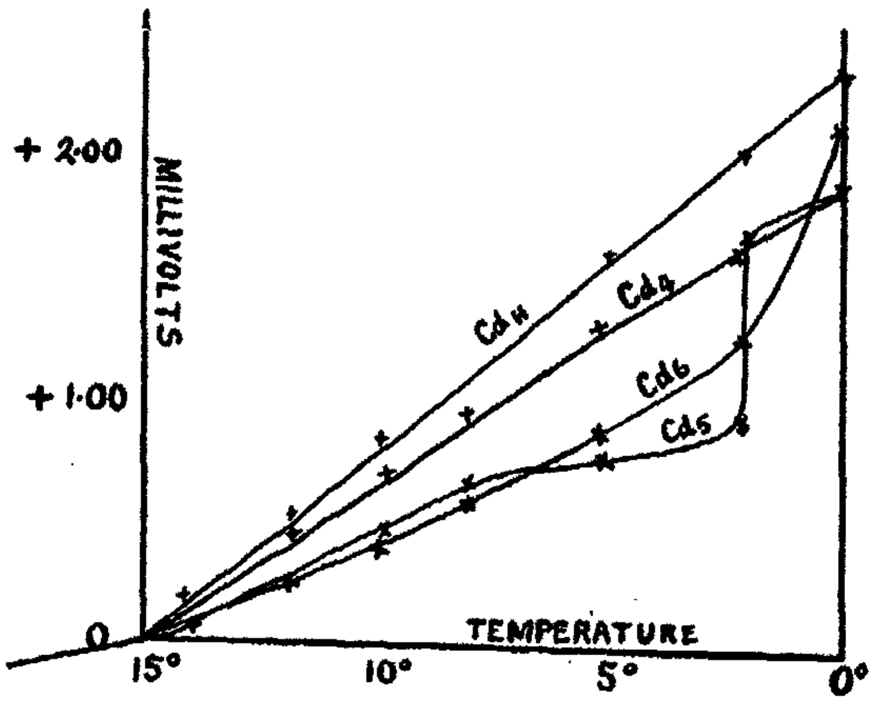

Fig. 2
Inversion of cadmium sulphate in the Weston cell

below 15°, which were sufficient to satisfactorily verify the observations already given.

Ratio of Clark to Cadmium

Not a little interest is attached to a determination of the ratio of the Clark to the Weston cell on account of the recent discussion of the absolute value of the Clark cell, which has such an important bearing on the absolute value of the mechanical equivalent of heat deduced by the electrical method of calorimetry. Dr. Kahle[1] has recently made some determinations of this ratio by means of the standard cells in the possession of the Reichsanstalt. The value of the ratio from a direct comparison of the Clark cell at 15° to the cadmium cell at 20° is given by him to be

$$\frac{\text{Clark } 15^\circ}{\text{Cad } 20^\circ} = 1.40663.$$

A comparison of cells Cd_3, Cd_4, Cd_5 and Cd_H with the B. O. T. "crystal" Clark cells described by the writer in another place[2] was made by means of the cylinder potentiometer and the 6000-ohm galvanometer, which were used in some preliminary experiments on the comparison of the Clark cells.[3] This potentiometer was repeatedly calibrated and its errors determined.

Table IV contains the results of this comparison on the cells, which were all maintained at a constant temperature near 15° C.

TABLE IV

March 6, 1897

Cell	Potentiometer reading corrected to 15°	Potentiometer reading corrected for uniformity
X_1	68225	68290
Cd_3	48453	48575
Cd_4	48460	48582
Cd_5	48458	48580
Cd_H	48460	48582

Correcting the reading of X_1 to the mean of the "crystal"

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[1] Wied. Ann. 67, 35 (1899).

[2] Proc. Roy. Soc. 67, 151 (1897).

[3] loc. cit. p. 121.

cells and reducing the mean cadmium reading to 20° by the formula

$$E_t = E_{15} - 0.086\,(t - 15),$$

the ratio of Clark to Weston is

$$\frac{\text{Clark } 15^\circ}{\text{Cad } 20^\circ} = \frac{68294}{48558} = 1.40644,$$

a value only slightly different to that given by Dr. Kahle.

McGill University,
April 6, 1900

NOTE ADDED MAY 22, 1900

Since sending in the account of the measurements given above of the ratio of the Clark cell to the Weston, the author has had occasion to summarize all the data relative to the comparison of the original B. O. T. "crystal" Clark cells, used in finding the ratio, which have been in the possession of the laboratory since 1895, with numerous other sets of cells made at different times since then. It has been found that the mean value of these original cells is systematically lower by 0.14 millivolt or 1 part in 10,000 than the means of all the other sets of cells, all of which agree very closely with each other. If full weight be given to these latter cells then the value of the ratio of Clark to Cadmium is increased to 1.40658. This value is so nearly identical with the value found for the ratio of the cells in the possession of the Reichsanstalt as to be, if not a coincidence, at least an indication of the great accuracy attainable in the preparation of these standard cells by independent observers.

ON THE ELECTROLYTIC DEPOSITION OF METALS FROM NON-AQUEOUS SOLUTIONS

BY LOUIS KAHLENBERG

In connection with my researches on the differences of potential between metals and non-aqueous solutions of their salts[1] it was necessary to ascertain whether Faraday's law holds for such solutions, before attempting to apply Nernst's formula for calculating the E. M. F. of the galvanic chains investigated. A series of electrolytic determinations was consequently made, the results of which are of general interest because little or nothing has hitherto been done on the electrolytic deposition of the metals from other than aqueous solutions at ordinary temperatures. The reason for this probably lies in the fact that it is commonly supposed that non-aqueous solutions do not conduct electricity sufficiently to admit of electrolytic determinations.

The general plan of experimentation was as follows: A known quantity of anhydrous salt was dissolved in a definite amount of anhydrous solvent. This solution was then electrolyzed, using a platinum cathode and an anode of the same metal whose salt the solution contained. The difference of potential between the electrodes was ascertained in each case, as was also the area of the cathode. The amount of metal deposited was compared with the silver separated out in a silver voltameter that was placed in the same circuit. The voltameter, of course, also indicated the strength of the current used. An aqueous solution of silver nitrate 1 to 7 was used in the voltameter. The temperature of experiment was about 20° C unless otherwise stated.

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[1] Jour. Phys. Chem. 3, 379 (1899).

A *n*/10 solution of silver nitrate in pyridine when thus electrolyzed for one and one-fourth hours, using a difference of potential of two volts between the electrodes and a cathode of 15 sq cm area, yielded a deposit of 0.3827 g silver. The deposit in the voltameter weighed 0.3849 g. In another experiment, the same solution was electrolyzed for one hour, using a pressure of two volts and a cathode having an area of 60 sq cm. The deposit weighed 0.7819 g; that in the voltameter weighed 0.7836 g. In each case the deposit from the pyridine solution was white, firm, compact, well adhering, and susceptible to polish. It was then not unlike the deposits obtained from the cyanide solutions commonly used in silver plating.

A *n*/10 solution of silver nitrate in aniline was electrolyzed for five hours, the cathode area being 60 sq cm and the difference of potential between the electrodes two volts. The silver deposited weighed 0.1780 g, while that separated out in the voltameter weighed 0.1788 g. The deposit from the aniline solution was white, dense, and well adhering.

Silver nitrate in benzonitrile (0.8585 g in 10 cc) was electrolyzed for thirty-four minutes, using an E. M. F. of 1.9 volts and a cathode of 15 sq cm area. The silver deposited was white, firm, dense, and well adhering. It weighed 0.1603 g, while that deposited in the voltameter weighed 0.1612 g.

A saturated solution of silver nitrate in quinoline was electrolyzed for four and one-quarter hours, employing an E. M. F. of two volts and a cathode having an area of 60 sq cm. The deposit weighed 0.2452 g, while that in the voltameter weighed 0.2501 g. The silver deposited from the quinoline solution appears very dark at first, owing to the presence on it of carbonaceous decomposition products from the quinoline. The deposit after being washed with alcohol and strongly heated turns white; it is firm, compact, and well adhering. The appearance of the carbonaceous material on the silver indicates that a complicated reaction takes place at the cathode to a certain extent. To this the fact that the silver deposited weighed appreciably less than that thrown down in the voltameter is very likely to be ascribed.

A solution of lead nitrate in pyridine, containing 4.4335 g of the salt in 50 cc, was subjected to electrolysis at 50° C for five hours and seventeen minutes, using a cathode 15 sq cm in area and an E. M. F. of three volts. The deposit was grayish, well adhering, and weighed 0.0732 g. The silver in the voltameter weighed 0.0745 g, which is equivalent to 0.0714 g lead. The solution is a very poor conductor as is evident from the slight deposit obtained.

A fourteen percent solution of antimony trichloride in methyl alcohol was electrolyzed for one hour, using a cathode of 20 sq cm area and an E. M. F. of 1.8 volts. The antimony, which was deposited in bright, not very well adhering crystals, weighed 0.2239 g, while the silver precipitated in the voltameter weighed 0.6156 g, which is equivalent to 0.2280 g antimony. In the second experiment, which was run for two hours and sixteen minutes under the same conditions as above, except that an extra resistance was introduced into the circuit, 0.2146 g of antimony was deposited and 0.5915 g silver was separated out in the voltameter, the latter amount being equivalent to 0.2192 g antimony. In this case, the antimony deposited was also crystalline and did not adhere very well. Several attempts to secure a good deposit of bismuth from a solution of bismuth trichloride in methyl alcohol failed, a black, spongy, poorly adhering mass being invariably obtained.

From a saturated silver nitrate solution in acetone, a dense, white, firmly adhering deposit may be obtained, but the solution conducts so very poorly that no quantitative determinations were made. It will be noted that, except in the case of the lead deposited from the solution of lead nitrate in pyridine, the silver separated out in the voltameter is somewhat larger in amount than it should be to conform strictly to Faraday's law. The most notable discrepancy occurs in the case of the quinoline solution which has already been discussed. The silver nitrate solution used in the voltameter was one that had been repeatedly employed, and according to Rodger and Watson,[1] such solutions

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[1] Rodger and Watson: Phil. Trans. 186A, 631 (1895).

give deposits that are somewhat too heavy. The silver deposits obtained from the silver nitrate solutions in pyridine, benzonitrile, and aniline were somewhat brownish in color when first taken from the solutions; only after being washed with alcohol and heated did they assume the fine white appearance. Now this brownish discoloration was not as great as in the case of the quinoline solutions; but nevertheless it indicated that, like in the latter, the solvents had suffered some decomposition. It is to these slight side reactions that I am inclined to ascribe in the main the fact that a little less metal was deposited in the electrolytic cell than there ought to have been, according to the weight of the silver thrown down in the voltameter placed in the same circuit. The antimony deposited from the solution of antimony trichloride in methyl alcohol was perfectly bright and there were no indications whatever of side reactions; nevertheless it will be noted that in both of the experiments above described, the antimony deposited is not quite equivalent to the silver obtained in the voltameter. As the two separate determinations agree fairly well, I shall content myself with the presentation of the results obtained, adding simply that the antimony used was a so-called C. P. sample obtained in the market and was not further tested as to its purity.

Aside from the minor discrepancies alluded to, the results recorded taken in general, go to show that Faraday's law does hold for non-aqueous solutions. The work done thus far is to be considered as preliminary in character.

The question arose, can silver nitrate be completely deposited from a silver nitrate solution in pyridine by using two platinum electrodes, and if so, under what conditions? It would also be of interest to know whether silver can be completely deposited in compact form from a solution of silver nitrate in pyridine plus water, and under what conditions. The investigation of these questions was undertaken in this laboratory by Mr. W. C. Sieker, and the results that were obtained are given in the following table, the headings of which are self-explanatory. All the determinations were made at room temperatures (about 20° C).

Grams $AgNO_3$ taken	Ag calculated	Ag found	E. M. F. in volts	Current in milli amp per 100 sq cm cathode	Time	Condition of deposit	Solvent
0.6281	0.3988	0.3970	2.08	285	9 h 35 m	compact	Pyridine
1.2790	....	....	4.14	...	1 " 40 "	spongy	"
1.2762	0.8103	0.8103	2.12	...	19 " 30 "	compact	"
0.6227	....	....	2.16	403	6 " 7 "	spongy	50% pyridine by volume
0.6072	0.3855	0.3823	2.16	172	5 " 40 "	compact	" " " "
0.6030	0.3828	0.3841	1.68	217	18 " 10 "	"	25% " " "
0.6240	0.3962	0.3960	1.68	211	7 " 30 "	"	" " " "
0.6342	0.4026	0.4023	1.56	238	7 " 55 "	"	12½% " " "
0.6136	0.3896	0.3898	1.28	255	8 " 10 "	"	10% " " "
0.5768	0.3663	0.3663	1.56	236	9 " 10 "	"	5% " " "
1.1458	0.7276	0.7264	1.28	178	13 " 25 "	"	[1] 5% " " "
0.6031	0.3829	0.3829	1.24	241	5 " 20 "	"	[2] 5% " " "
0.4862	....	....	1.16	231	3 " 30 "	spongy	[3] 2½% " " "
0.4618	0.2932	0.2930	1.52	201	22 " 10 "	compact	10% acetone " "
0.4650	0.2953	0.2850	1.64	956	1 " 50 "	"	Water saturated with aniline
0.5568	0.3536	0.3369	2.04	54	12 hrs	"	" " " "

[1] This solution contained 1 mol $AgNO_3$ to 3 mols pyridine.

[2] " " " 1 " " " 2 " "

[3] " " " 1 " " " 1 " "

The solutions electrolyzed usually had a volume of about 50 cc. The times do not indicate the minimum time required to throw down all the silver. Owing to the press of other work, the experiments usually were allowed to run longer than was actually necessary.

It will be observed from the table that silver can be completely deposited in compact form from a silver nitrate solution in pyridine. The potential used should be about three volts and the current density about 0.3 ampere per 100 sq cm cathode area. Again, silver can be completely deposited in dense, white form from a silver nitrate solution in pyridine, plus water, providing that at least two molecules of pyridine are present to one of silver nitrate. Good results are obtained when employing an E. M. F. of 1.24 to 2.16 volts, and a current density of from 0.17 to 0.25 ampere per 100 sq cm cathode area. The table also shows that silver may be deposited in a dense, compact form, quantitatively from a silver nitrate solution in a solvent consisting of nine volumes of water and one volume of acetone. Finally, when silver nitrate is dissolved in water previously saturated with aniline, the deposit that is obtained upon electrolysis is not crystalline, but dense and compact. The quantitative results obtained with the two solutions tested were not very satisfactory as the table shows. On standing, the aniline gradually reduces the silver nitrate. This process is of course very much accelerated when the solution is exposed to the light.

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VAPOR-PRESSURE RELATIONS IN MIXTURES OF TWO LIQUIDS, II

BY A. ERNEST TAYLOR

In the previous part of this article, the methods of determining vapor-pressures and boiling-points have been discussed in detail. The next thing to consider is naturally the numerical results obtained with the use of the apparatus described. The present paper will concern itself almost solely with a recording of the data which I observed, first with regard to the vapor-pressures of solutions of acetone and water at various temperatures, and secondly with regard to the composition of the vapor given off under similar conditions.

The first set of measurements are given in Tables I–XIII, the second in Table XIV. The tables do not contain carefully selected data, but they record the measurements as actually made in the series. A few of the first sets have been discarded, and possibly half a dozen individual measurements have been omitted which evidently contained large errors in reading. It will be noted that at low temperatures the temperature rises rapidly with the pressure. These measurements were in consequence very hard to make, and probably contain a much greater error than the average measurements. The greater the percentage of water the greater is the change of the temperature with the change of pressure. The ten and twenty percent acetone solutions were therefore much more difficult to measure than the rest, and their vapor-pressure relations must assuredly be less accurately determined than those of the solutions richer in acetone.

Whenever with slight increase of pressure the temperature rises rapidly, it is almost impossible to make very accurate measurements. The reason for this is, that it is so very difficult to keep the temperature constant for any length of time. To make accurate readings it is necessary that the temperature should remain essentially unchanged for ten or fifteen minutes, for equilibrium cannot be established much sooner. Any slight leak will raise the boiling-point and perhaps make it necessary to raise the temperature of the bath, which will also in turn raise the pressure and consequently the boiling-point. This then explains very completely why some rather large discrepancies are to be noticed at the lower temperatures and in those solutions containing a very large percent of water.

Table I contains the measurements made of the vapor-pressure of pure water. In the table they are compared with those of Regnault recalculated by Broch[1] as found in Landolt and Börnstein's Tabellen. The agreement is fairly good and is easily within my experimental error. In my further work I have used the figures of Regnault, as being measured much more accurately than was possible with my apparatus. Tables II–X contain my measurements with aqueous acetone solutions varying from ten to ninety percent by weight of acetone. Table XI contains similar measurements with pure acetone and at the end the measurements of Regnault. At the lower temperatures my measurements agree well with those of Regnault, but at high temperatures there is a greater discrepancy. These measurements with pure acetone are not difficult to make, and in subsequent work I have preferred to use my own measurements.

The measurements recorded in Tables I–XI were plotted on a large scale as a temperature-pressure diagram, the temperatures being measured along the abscissa and the pressures along the ordinate. Each tenth of a degree corresponded to one millimeter and each millimeter pressure to half a millimeter on the diagram. Fig. 1 represents this diagram on a small scale. Through the points thus plotted, it was found possible to pass smooth curves for the various solutions. Most of the points lay well on the curves, but in some few cases a much greater error than is desirable came in.

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[1] Trav. et Mem. du Bur. internat. des Poid et Mes. 1A, p. 33' 1881.

The curve at the bottom of the diagram is that for pure water, the next that for ten percent acetone, the next twenty percent, and so on, the highest curve being that for pure acetone. It will be noticed that the pitch of the acetone curve is very much greater than that of the water curve, and that the change from one to the other is made gradually through the various solutions. At low temperatures the curves come very close together and spread out rapidly at higher temperatures. At any one fixed temperature the effect of adding a little acetone to the water is very noticeable in the rapid rise of the pressure, as for instance in going from pure water to ten percent and then to twenty percent acetone. After thirty percent, the rise in pressure is comparatively small. In the same way starting from pure acetone the fall in pressure to ninety percent is much greater than that from ninety to eighty. These two effects from the water end and from the acetone end meet somewhere at about sixty percent, the change in pressure from fifty to sixty percent acetone and from sixty to seventy percent acetone being the smallest. These curves were extended somewhat beyond the actual readings made, so that they all go to 800 mm pressure and as low as 25° C temperature.

From the curves in Fig. 1, the data in Table XII was compiled. This table contains the temperatures obtaining at constant pressures, which range from 100 mm to 800 mm for the various solutions. The vertical columns have for headings the percentage acetone composition of the solutions, and the horizontal ones the constant pressures. This table, as it is taken from the curves in Fig. 1, should represent a careful averaging of all the data given in Tables I–XI.

The data from Table XII has been plotted as a series of constant pressure curves in Fig. 2. The temperatures are measured as abscissæ and the percentage concentrations of acetone as ordinates. The curve at the left is that for 150 mm pressure, the next for 200 mm pressure and so on up to 800 mm pressure. They form a series of very nearly parallel curves of rather peculiar shape. In the middle portion they approach

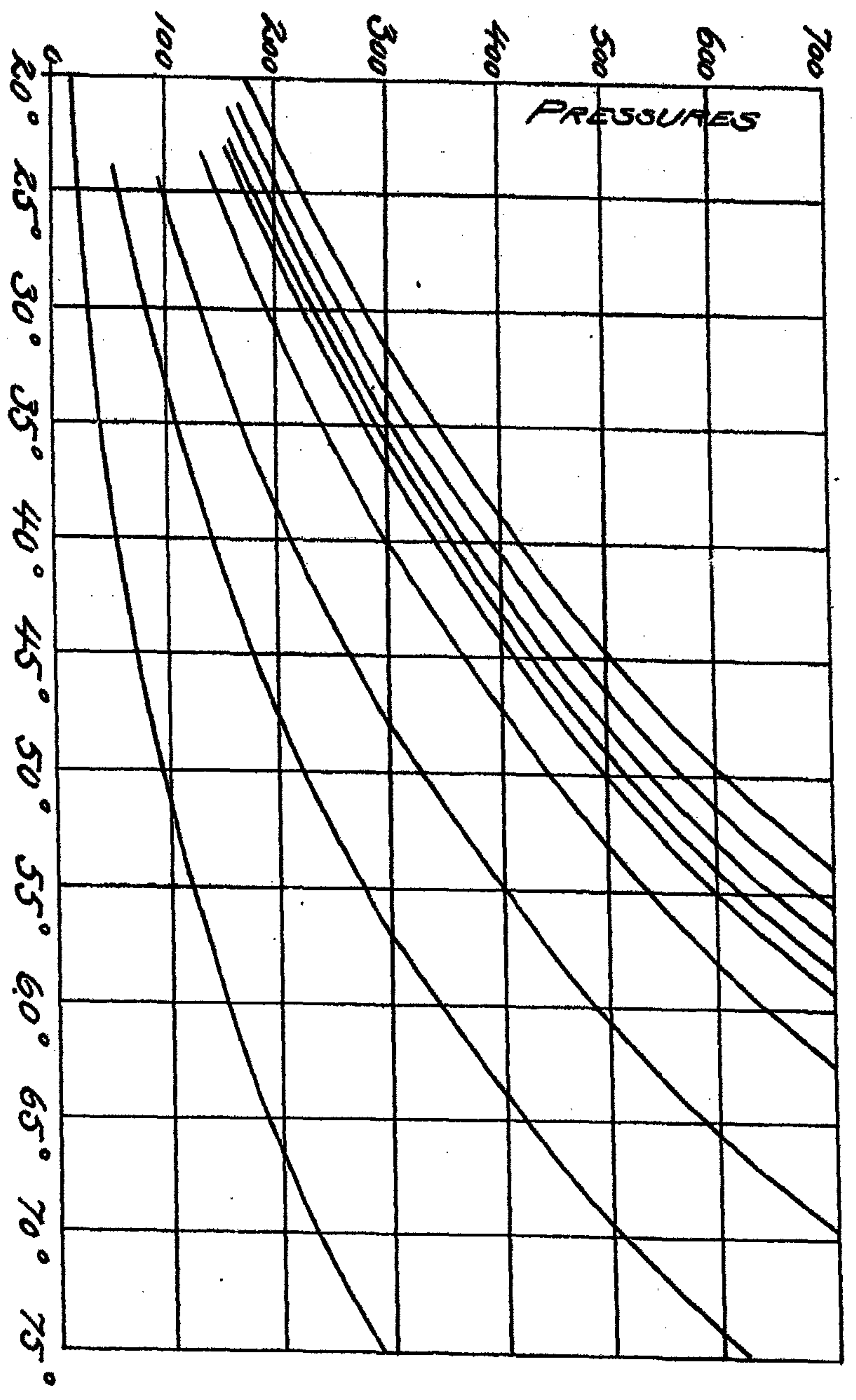
PRESSURES
0
100
200
300
400
500
600
700
20°
25°
30°
35°
40°
45°
50°
55°
60°
65°
70°
75°

Fig 1.

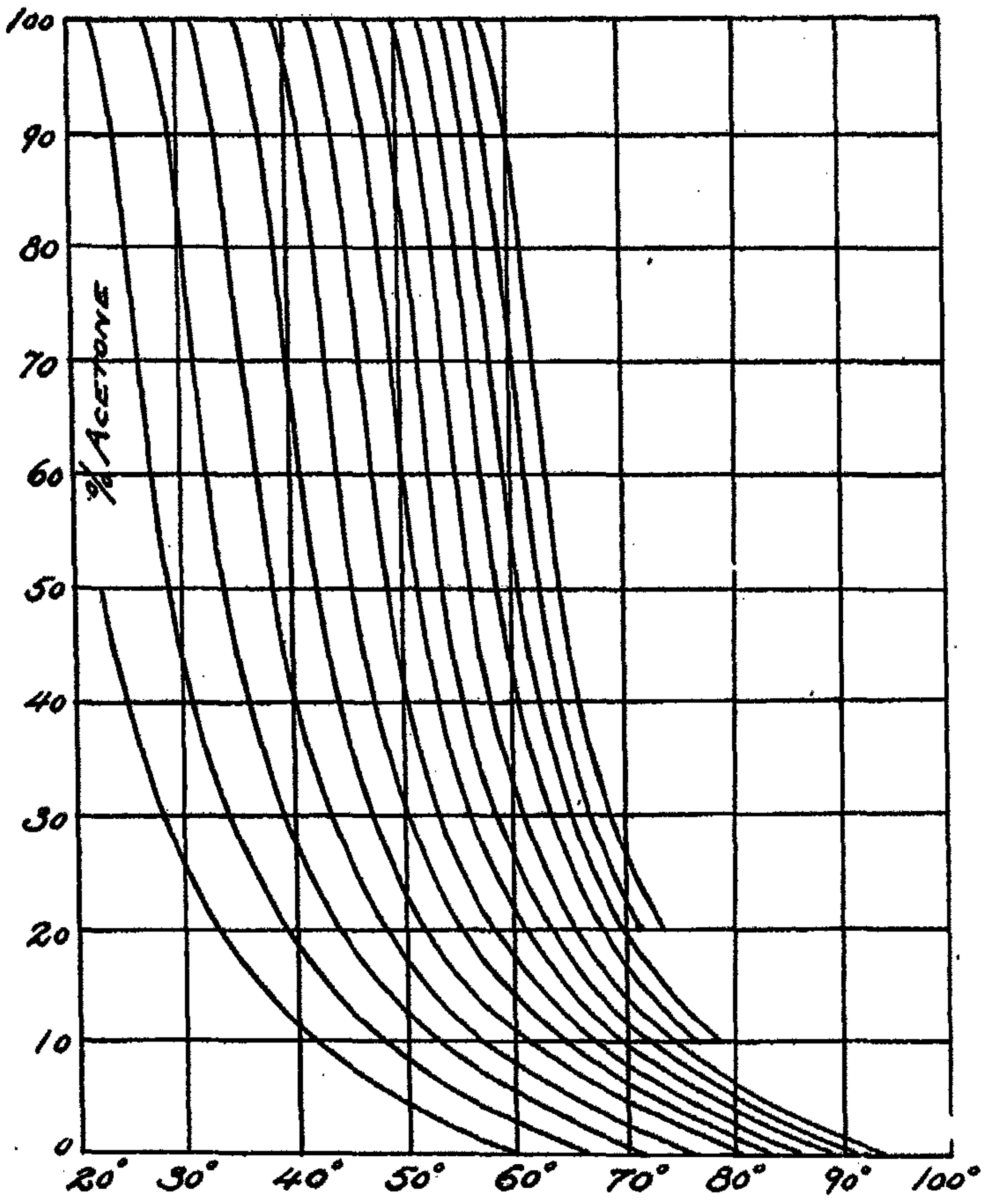

Fig. 2

very nearly to straight lines, but at the acetone and at the water ends there is a very decided change in the pitch of the curves.

Table XIII is a compiling from the curves in Fig. 1 of the pressures which obtain at constant temperatures. The data from this table is graphically expressed in a concentration-pressure diagram in Fig. 3. The concentrations are measured as abscissæ and the pressures as ordinates. The lowest curve represents the

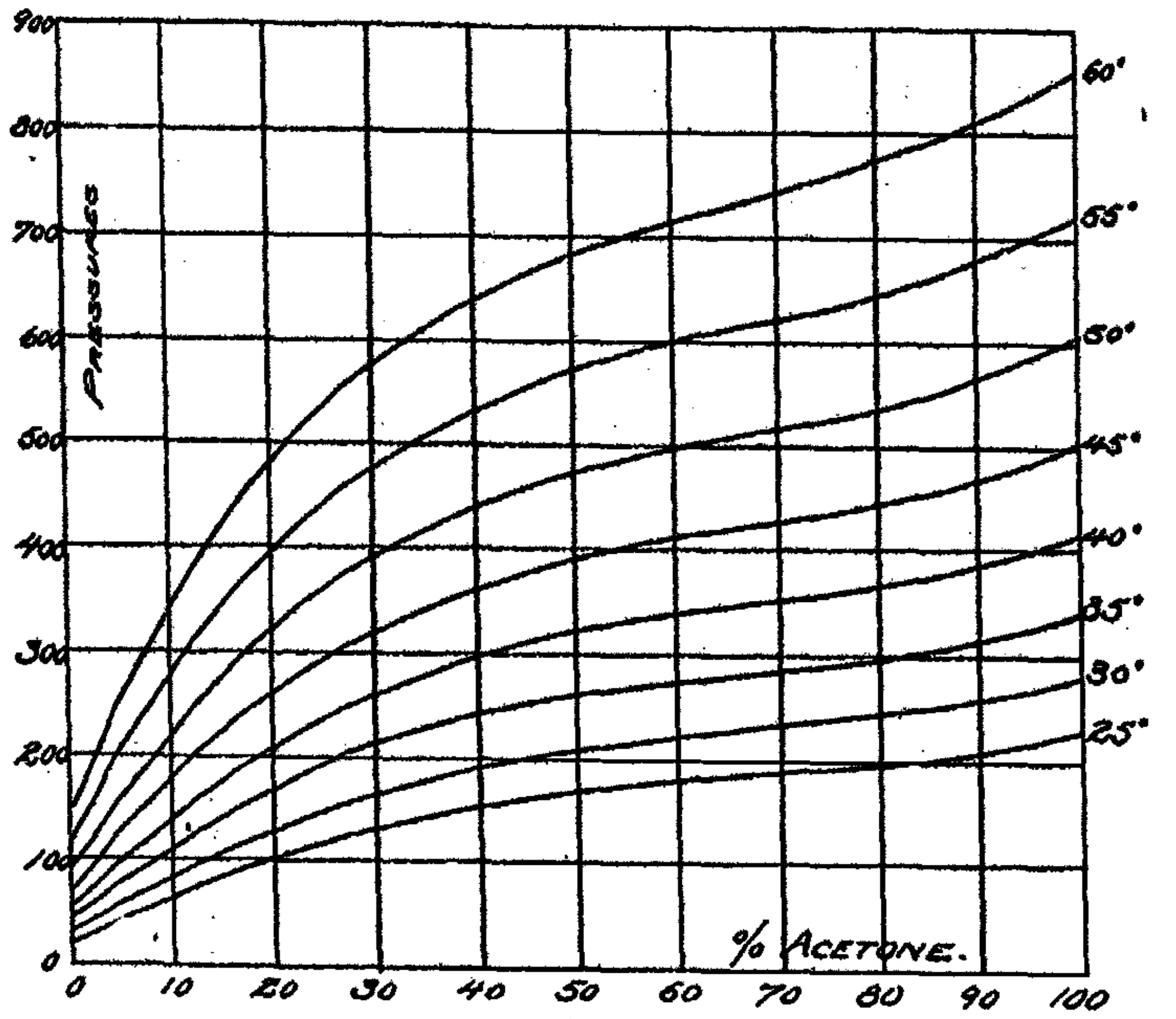

Fig. 3

pressure and concentration relations which exist at 25° C, the next curve represents similar relations at 30° C and so on by intervals of five degrees up to 60° C. These curves start very close together at the pure water line, the pressures rapidly rising with increase of acetone, then more slowly, and from about sixty-five percent acetone again more rapidly, the curve radically changing its form at this point.

The next thing to consider is the composition of the vapor given off from the various solutions. As previously described, 220 cc of solution was taken each time and 20 cc distilled over, and its composition determined from its boiling-point. It was found that the vapor composition varied but little with the change in pressure, so each solution was distillled at but two different pressures, viz. atmospheric and at 200–250 mm pressure. The results obtained are given in Table XIV. In the first column A are given the percentage compositions of the so-

TABLE I

Water

Press mm	B Pt	Press mm	B Pt	Press mm	B Pt	Press mm	B Pt
19.7	20.8°	49.5	38.7°	117.5	55.0°	203.5	67.1°
20.5	22.1	66	43.4	124.5	56.5	238	70.4
23.0	23.8	70	44.7	128.5	57.1	242.5	71.0
23.5	25.4	74.5	46.0	135.5	58.2	287	74.9
25.5	27.1	85	48.6	141.5	59.1	289	75.1
27.5	28.1	88	49.4	146.5	59.9	355	80.0
34.5	31.7	92.5	50.2	149.5	60.3	357	80.3
38.5	33.2	98	51.5	158.5	61.3	365.5	80.8
40.5	34.2	103	52.4	161.0	61.9	438.5	85.4
42.5	35.4	105	52.8	164.5	62.2	440.5	85.5
44	36.2	107	53.2	195.7	66.0	517.5	89.85
46	37.2	116	54.9	200.5	66.55	540.5	90.75
		Regnault				631.5	94.85
17.36	20.0	49.26	38.0	135.57	58.0	327.05	78.0
19.63	22.0	54.86	40.0	148.88	60.0	354.87	80.0
22.15	24.0	61.02	42.0	163.29	62.0	384.64	82.0
24.96	26.0	71.36	45.0	187.10	65.0	433.19	85.0
28.06	28.0	83.19	48.0	213.79	68.0	486.76	88.0
31.51	30.0	91.98	50.0	233.31	70.0	525.47	90.0
35.32	32.0	101.55	52.0	254.30	72.0	566.71	92.0
41.78	35.0	117.52	55.0	288.76	75.0	633.66	95.0

TABLE II

10% Acetone

Press mm	B Pt	Press mm	B Pt	Press mm	B Pt	Press mm	B Pt
128.5	38.2°	344.5	60.4°	143	40.4°	295.5	56.6°
143	40.7	396.5	63.55	145	41.0	348	60.8
145	40.9	446	66.6	145	41.1	352	60.9
146	41.1	506	70.0	147	41.3	404	64.3
174	44.5	507.5	70.2	181	45.5	405	64.3
173.5	44.6	543.0	72.0	183	46.0	452.5	67.1
198.5	47.5	600.5	74.3	186.5	46.2	453.5	67.1
200.5	47.7	596.5	74.1	200	47.7	497.5	69.1
226.5	50.6	652	76.3	202	48.0	499	69.3
226.5	50.6	652	76.2	231	50.9	551	71.6
251	52.9	697.5	78.3	233	51.1	595.5	73.6
252	53.0	695.5	78.05	262.5	54.2	597.5	73.8
276	55.0	695.5	77.9	258.5	53.5	650	76.1
278	55.3	739.2	80.0	258.5	53.6	695.5	78.5
300	56.9	739.2	79.8	278.5	55.3	695.5	78.4
302	57.0	——	——	282	55.5	742	80.05
342.5	60.3	——	——	295.5	56.6	742	79.9

TABLE III

20% Acetone

Press mm	B Pt	Press mm	B Pt	Press mm	B Pt	Press mm	B Pt	Press mm	B Pt
117	27.2°	497.5	60.7°	195	38.2°	644	67.1°	400	55.1°
126	29.5	498.5	60.8	196	38.4	645	67.1	445.5	57.8
128	29.8	542.5	63.0	233	42.2	712	69.7	445.5	57.7
140.5	31.7	542.5	62.9	237	42.6	716	69.9	496.5	60.7
141.5	31.9	598.5	65.55	249.5	43.7	743.7	71.2	547.5	63.05
144	32.4	598.5	65.6	251.5	43.8	159.5	34.1	549.5	63.1
147	32.7	636	67.1	277	46.0	163	34.7	601.5	65.9
173.5	36.2	646	67.55	279	46.2	164	35.0	602.5	65.8
177.5	36.6	647	67.65	301	48.0	196.5	38.6	660	68.0
198.5	39.2	692.5	69.4	349.5	51.7	198.5	38.7	701.5	69.7
253	44.5	693	69.4	397.5	54.8	198.5	38.75	705	69.9
257	44.7	730.5	70.7	399	54.9	225	40.5	703	69.8
295	48.0	121.5	28.1	448	57.9	249	43.8	739	71.1
296	48.0	127.5	29.1	449.5	58.0	247.5	43.7	—	—
354	52.2	131.5	30.2	498.5	60.7	274	46.1	—	—
356	52.4	133.5	30.6	499.5	60.7	275.5	46.2	—	—
357	52.5	136	30.9	548.5	63.0	302	48.2	—	—
395.5	54.9	159.5	34.1	549.5	63.05	303	48.3	—	—
446	57.7	162.5	34.4	598.5	65.2	344	51.5	—	—
447	57.9	164.5	34.9	598.5	65.25	400	55.0	—	—

TABLE IV

30% Acetone

Press mm	B Pt	Press mm	B Pt	Press mm	Bt Pt	Press mm	B Pt
148.5	27.9°	302	43.7°	453.5	53.6°	698	65.3°
156.6	29.1	303	43.7	501.5	56.2	737	66.6
161.5	29.6	351.5	47.2	502.5	56.2	—	—
178.5	31.7	346.5	46.95	549.5	58.6	—	—
178.5	31.8	333	45.95	601.0	61.2	—	—
187.5	32.8	337	46.3	602	61.2	—	—
191.5	33.4	402.5	50.6	603	61.25	—	—
196.5	33.8	403.5	50.6	650	63.2	—	—
243	38.9	449.0	53.4	651	63.3	—	—
245	39.1	451.5	53.55	700.5	65.3	—	—
251	39.5	—	—	—	—	—	—
253	39.6	—	—	—	—	—	—

TABLE V

40% Acetone

Press mm	B Pt	Press mm	B Pt	Press mm	B Pt	Press mm	B Pt
176	27.6°	734.8	63.7°	306.5	40.7°	544	55.5°
186	28.8	157	25.6	307.5	40.85	596	57.9
191.5	29.6	165.5	26.6	351.5	44.2	599	58.0
344.5	43.6	176.0	28.1	353.5	44.3	645.5	60.3
348.5	43.8	180.5	28.6	404.5	47.7	646.5	60.3
451.5	50.3	183	28.8	406	47.75	690.5	62.2
538	55.0	184	29.1	448.5	50.4	694.0	62.25
540	55.3	193.5	30.2	449.5	50.4	718.5	63.1
639	59.9	199	30.8	524.5	54.5	718.5	63.05
643	60.0	245	35.7	527	54.65	738.5	63.8
641	59.9	252	36.2	543	55.45	—	—

TABLE VI

50% Acetone

Press mm	B Pt	Press mm	B Pt	Press mm	B Pt	Press mm	B Pt
181.5	26.6°	443	48.1°	172.5	25.7°	452.5	48.85°
192.5	27.8	525.5	52.7	176.5	26.1	496.5	51.3
204.5	29.2	526.5	52.7	203.5	29.3	498	51.4
212.5	30.3	627.5	57.7	205.5	29.4	548	53.9
222.5	31.4	626.5	57.6	252.5	34.3	597	56.2
227.5	31.8	730	61.9	254.5	34.6	648	58.5
313	39.4	730	61.85	309.5	39.4	647.5	58.45
315	39.6	146.5	22.1	314.0	39.6	693	60.5
318	39.7	152.5	22.8	349	42.2	745.3	62.5
316.5	39.7	157.5	23.6	401.5	45.8	—	—
437	47.9	161.5	24.1	406	46.0	—	—
441	48.0	169.0	25.2	449.5	48.8	—	—

TABLE VII

60% Acetone

Press mm	B Pt	Press mm	B Pt	Press mm	B Pt	Press mm	B Pt
199.5	27.3°	620	55.9°	227	30.2°	453	47.4°
202.5	27.6	623	56.1	228.5	30.4	500	50.1
206.5	27.8	625	56.2	244.6	32.1	550.5	52.65
209.5	28.1	735.5	60.85	246	32.2	550.5	52.7
297.5	36.8	156.5	21.6	297.5	36.7	607	55.3
299.5	36.9	159.5	22.1	300	36.9	642.5	56.9
301.5	37.0	161	22.5	351	40.9	643.5	57.0
397.5	43.9	165	23.0	352	40.9	696.5	59.2
399.5	44.0	168	22.4	396	43.9	701.5	59.4
502	50.2	198.5	27.0	398	44.0	739	61.0
504	50.2	200.5	27.35	450	47.2	—	—

TABLE VIII

70% Acetone

Press mm	B Pt	Press mm	B Pt	Press mm	B Pt	Press mm	B Pt
196.5	25.9°	505	49.4°	190	25.1°	458.5	46.8°
208.5	27.0	507	49.5	213.5	27.6	459.5	46.95
215.5	27.9	592.5	53.7	216.5	28.1	504.5	49.3
228.5	29.4	595	53.8	222.5	28.85	506.5	49.4
257.0	32.2	674	57.5	251.5	31.7	555	51.95
260	32.4	680	57.7	254.5	32.0	556	52.0
298	35.7	684	57.8	305	36.25	602	54.1
298.5	35.8	729.5	59.7	307.5	36.5	604	54.2
301.5	36.0	163.5	21.7	351.5	39.95	649.5	56.2
395	42.9	177.5	23.8	354.7	40.2	695	58.1
399	43.1	181	24.1	400	43.3	696	58.1
502.5	49.2	186.5	24.7	404.5	43.5	748.5	60.3

TABLE IX

80% Acetone

Press mm	B Pt	Press mm	B Pt	Press mm	B Pt	Press mm	B Pt
176	22.3°	406	42.5°	746	59.0°	405	42.4°
183.5	23.4	464	46.0	170.5	21.6	407.5	42.6
189.5	24.1	466.5	46.1	174.5	22.1	456.5	45.6
193.5	24.5	468	46.2	175.5	22.3	458.5	45.7
200	25.2	499.5	48.0	194	24.4	510.5	48.6
253	30.9	502.5	48.2	195	24.5	513	48.8
262	31.6	548.5	50.6	220	27.5	516.5	48.9
268	32.2	550.5	50.7	250	30.6	551.5	50.7
299	34.8	552.5	50.75	251.5	30.7	554	50.8
302	35.1	596.5	52.8	280.5	33.3	609	53.3
307	35.4	599.5	53.0	281.5	33.35	650.5	55.2
355	39.0	644.5	55.0	310	35.8	691.5	56.9
357.5	39.2	647.5	55.1	312	36.0	742.2	58.9
359	39.4	647.5	55.0	317.5	36.3	—	—
398	41.9	687.5	56.7	357	39.2	—	—
403	42.3	689.5	56.8	360	39.4	—	—

TABLE X

90% Acetone

Press mm	B Pt	Press mm	B Pt	Press mm	B Pt	Press mm	B Pt
191.5	23.1°	464.5	44.7°	181	22.0°	452	44.0°
196.5	23.6	531.5	48.4	188	22.6	496	46.5
208.5	25.1	533.5	48.4	194.5	23.4	498	46.5
213.5	25.7	558.5	49.6	197	23.6	557.5	49.5
214	25.6	560.5	49.7	224	26.5	558.5	49.6
216	25.8	610.5	52.0	254	29.6	592.5	51.2
255	29.8	612.5	52.1	252	29.4	642	53.4
254	29.6	615	52.2	254	29.6	693	55.5
263	30.5	643	53.4	276.5	31.6	693	55.4
305.5	34.1	645	53.5	277.5	31.7	745.7	57.6
308.5	34.3	709.5	56.2	296.5	33.5	745.7	57.7
311	34.4	715.5	56.4	347.5	37.3	—	—
346	37.35	737.5	57.3	348.5	37.35	—	—
350	37.45	—	—	395.5	40.5	—	—
396	40.6	—	—	400	40.8	—	—
398	40.7	—	—	403	40.9	—	—
458.5	44.4	—	—	450	43.9	—	—

TABLE XI

Acetone

Press mm	B Pt	Press mm	B Pt	Press mm	B Pt	Press mm	B Pt
188.5	20.7°	347	35.2°	647	51.7°	398	38.8°
192.5	21.1	348	35.3	603	49.7	445	41.7
194.5	21.3	397.5	38.5	615	50.2	498.5	44.7
195	21.45	399.5	38.7	640.5	51.5	547	47.2
197	21.7	403.5	39.1	642.5	51.6	548	47.3
218	23.9	498	44.6	695.5	53.9	599.5	49.8
222	24.3	506	44.9	697.5	54.0	601	49.8
254.5	27.6	507.5	45.0	697.5	54.05	650	52.0
261.5	28.2	548.5	47.2	737.5	55.6	698.5	54.1
295	31.2	554.5	47.5	318	33.1	700	54.2
301	31.7	593.5	49.4	353.5	35.7	739.5	55.7
308	32.3	596.5	49.5	355.5	35.9	—	—
345	35.0	645	51.7	397	38.7	—	—
Regnault							
179.6	20.0	420.1	40.0	860.5	60.0	—	—
281.0	30.0	620.9	50.0	1189.4	70.0	—	—

TABLE XII

Temperatures

(At constant pressure)

Press mm	0	10	20	30	40	50	60	70	80	90	100
100	51.7°	33.7°	—	—	—	—	—	—	—	—	—
150	60.2	41.6	33.0	28.05	24.9	22.6	—	—	—	—	—
200	66.5	47.7	39.0	34.3	31.0	28.8	27.35	26.35	25.2	24.1	21.95
250	71.6	52.85	43.9	39.35	36.05	34.1	32.6	31.5	30.5	29.2	27.1
300	75.9	57.1	48.2	43.5	40.2	38.4	36.9	35.9	34.9	33.6	31.65
350	79.65	60.8	51.8	47.15	44.0	42.3	40.75	39.8	38.6	37.45	35.5
400	83.0	64.05	55.05	50.4	47.3	45.6	44.1	43.3	42.15	40.9	38.9
450	86.0	66.95	58.0	53.45	50.4	48.7	47.2	46.3	45.2	43.9	42.0
500	88.7	69.5	60.75	56.15	53.2	51.45	50.05	49.05	48.05	46.7	44.75
550	91.2	71.9	63.2	58.6	55.8	53.95	52.7	51.7	50.7	49.2	47.3
600	93.5	74.05	65.55	61.0	58.15	56.35	55.05	54.0	53.0	51.55	49.75
650	95.7	76.25	67.7	63.25	60.4	58.65	57.35	56.3	55.2	53.75	52.0
700	97.7	78.3	69.6	65.25	62.45	60.7	59.5	58.45	57.25	55.8	54.2
750	99.65	—	71.4	67.1	64.35	62.65	61.4	60.4	59.15	57.8	56.1
800	101.45	—	73.05	68.85	66.2	64.45	63.25	62.15	60.9	59.7	57.95

TABLE XIII

Pressures

(At constant temperature)

% Ac	60° mm	55° mm	50° mm	45° mm	40° mm	35° mm	30° mm	25° mm
0	149	117.5	92	71.5	55	42	31.5	23.5
10	339	275	221	177	139	107	82	65
20	483	399	324	262	209	165	130	104
30	577	478	393	319	258	206	164.5	130
40	640	534	442	364	298.5	239	191.5	151
50	682	572	472	391	319	260	211	168
60	714	598	499	414	340	277	224	180
70	740	621	517.5	428	352	290	235	188
80	774	645	536	447	368	301	245	198
90	808	680	566.5	469	387.5	318	258	209
100	860	721	607	505	416	343	281	229

lutions before distilling, in column A_1 the average composition of the solution during distillation. This is the average of the composition of the solution at the beginning and at the end of the distillation. Column V gives the percentage acetone composition of the vapor given off, and V_1 the composition of the vapor which would be given off by the original solution if its composition did not change. The results are obtained by plotting the original data and interpolating. In column P are given the pressures under which the distillations took place. (Atm is an abbreviation for atmospheric pressure, that being at this time about 740 mm). In column M are given the vapor compositions in molecular concentrations. They exactly correspond to column V_1. These molecular concentrations represent the number of molecular weights of acetone in one hundred molecular weights of vapor.

The first thing which one notices in looking over this table is the large percentage of acetone given off in the vapor even of the ten percent solution. This makes the measurements difficult. As will be seen, in boiling off 20 cc of condensed vapor from 220 cc of 10 percent acetone solution, the composition of the solution changes from ten percent to three and a half percent.

There is sure to be introduced a considerable error, when the composition changes so markedly during distillation. This does not come in much with the higher concentrations, for while the twenty percent solution gives off a ninety percent vapor, the ninety percent solution gives off only a ninety-seven percent vapor. With change of pressure the composition does not change greatly, on the average about two percent for 500 mm change in pressure. The vapor compositions are given to the quarter percents, and are accurate to about one percent, although in some cases there may be as great an error as two percent. The boiling-point method of determining composition is not especially accurate. This with the great difference in composition of the vapor and liquid makes an accuracy of one percent about all that can be hoped for. On looking at column M, however, it will be seen that an error of one percent in V_1 will introduce a greater error in M. This is due to the great difference in the molecular

TABLE XIV

A	A_1	V	V_1	P mm	M
10	6.8	74	81	200	57
10	6.9	72.5	78	atm	52.5
20	16.6	88	89.8	200	73
20	16.7	85.5	87.3	atm	68
30	26.9	92.5	93	200	80.5
30	27	90	90.5	atm	74.8
40	37.3	93.5	93.8	200	82.3
40	37.45	91	91.3	atm	76.3
50	47.75	95.3	95.3	225	86.3
50	47.85	93	93	atm	80.5
60	58.25	94.5	94.5	250	84.3
60	58.35	93.5	93.8	atm	82.3
70	68.7	95.5	95.8	250	87.5
70	68.8	94.3	94.5	atm	84.3
80	79.15	97.3	97.3	250	91.8
80	79.25	95.5	95.5	atm	86.8
90	89.65	97.3	97.3	250	91.8
90	89.7	96	96	atm	88.3

weights of water and acetone, viz. 18–58. The partial pressure of the acetone in the vapor, of course, depends upon the relative number of molecular weights of acetone found in the vapor.

The numerical results will soon be followed by a theoretical consideration of the same.

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ON THE DETERMINATION OF TRANSITION TEMPERATURES

BY H. M. DAWSON AND P. WILLIAMS

The influence of temperature on the equilibrium of homogeneous systems is such that the variation of the latter can be represented as a continuous function of the temperature. In the case of heterogeneous systems the variation of the equilibrium is also represented as a continuous function of the temperature provided the various phases of the system remain intact. In many cases, however, such a heterogeneous system undergoes at a definite temperature a complete change whereby one of the phases of the system disappears and is replaced by a new one. Systems which are characterized by the existence of such a transition temperature at which the two forms are capable of existing together in stable equilibrium, have been given the special designation of "condensed systems" by van 't Hoff. Such a transition temperature corresponds to a multiple point on the diagram representing the solubility relationships of the system, the number of coexistent phases at this point for a system composed of n bodies being $n + 2$.

Several different methods have been employed for the investigation of such transition temperatures, e. g., the dilatometric and thermometric, depending upon the volume and thermal changes accompanying the transformation, the method of isothermal crystallization, which is of especial value in determining the qualitative nature of the change, and finally the so-called identity method. By application of this latter method, which depends upon the identity of the saturated solutions of the two systems transformable one into the other, at the transition temperature, various properties of the solution have been made use of as a means of determining transition temperatures.

The properties of the solution which have as yet been investigated with this object are the concentration, the vapor-pressure, the solution pressure, and the difference of potential between the solution and a reversible electrode.

In the choice of a property of the solution suitable for determination of transition temperatures according to the identity method, the essential considerations are the exactitude with which the property in question can be measured, the facility with which the determination of the value of the property can be carried out, and in many cases the avoidance of a reduction in the quantity of saturated solution as a result of the measurement.

The determination of the density and the electrical conductivity of the saturated solution appeared to offer convenient methods of measuring transition temperatures and the experiments contained in this paper were carried out with a view of ascertaining the suitability of these methods for such measurements. The results obtained from the measurement of the density of the saturated solutions are given first and afterwards those from the electrical conductivity.

The density method

To test the applicability of this method of determination, a series of measurements was carried out with Glauber's salt, the transition temperature of which has already been determined by several different methods. From solubility determinations of Mulder, Loewel, and Gay-Lussac the transition temperature is calculated to be 32.6°–33° C; by measurement of the vapor-pressure van 't Hoff and van Deventer found 32.6° C; by the solution pressure method Verschaffelt obtained 32.74° C and Cohen and Bredig, by determining the temperature coefficient of the electromotive force, obtained 33.2° C. Finally a very accurate determination by Richards and Churchill[1] by the ther-

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[1] Zeit. phys. Chem. 26, 690 (1898).

mometric method, gave 32.379° C (Hydrogen thermometer). The differences exhibited by the values obtained by the different methods are not great, but in view of the last-mentioned result, would all appear to be too high. It seemed necessary, therefore, as a control to determine the solubility simultaneously with the density of the saturated solution, which was possible without any special measurements, since the former only involved the evaporation of the solution pipetted in the latter determination. The saturated solutions were prepared by agitating suitable quantities of pure salt and water in a large thick-walled test-tube, provided with a screw-shaped stirrer set in rapid rotation by a turbine. The solubility tube provided with a tight-fitting cork, was placed in an Ostwald thermostat, the temperature of which was maintained within 1/20° C of that desired by means of a special form of regulator. The mean time of stirring amounted to about four hours. The density determinations were made by means of the capillary pipette described by Meyerhoffer and Saunders.[1] The latter had a capacity of about 5 cc, and, before introduction into the solubility tube for the purpose of pipetting, was heated to the temperature of the bath by placing for some time in a second tube immersed in the thermostat. After the pipette had been filled by suction it was again introduced into the second tube and left for some time before the level of the solution in the capillary was read off, whereby errors resulting from any small changes of temperature during the time required for pipetting were entirely avoided. Since the variation of solubility of the hydrated salt with the temperature is very considerable, the latter was maintained constant to 0.01° C for at least an hour previous to pipetting, a Beckmann thermometer being used for this purpose. After the density of the solution had been measured the contents of the pipette were carefully removed and the quantity of sodium sulphate determined. The following table gives the results so obtained. The thermometer used was a normal one corrected at the Physikalische Reichsanstalt in Charlottenburg.

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[1] Zeit. phys. Chem. 28, 466 (1899).

Temperature	Saturated solution of	Composition of solution: (*a*) parts per 100 water	Composition of solution: (*b*) mols Na_2SO_4 per 100 H_2O	Density
26.03°	Glauber's salt	——	——	1.2204
28.01	"	——	——	1.2499
29.93	"	——	——	1.2824
31.04	"	——	——	1.3030
31.94	"	47.83	6.062	1.3218
32.93	"	52.12	6.606	1.3445
32.06	Anhydrous Na_2SO_4	49.76	6.307	1.3324
33.23	"	49.53	6.279	1.3305
33.93	"	——	——	1.3294
34.33	"	——	——	1.3287
36.22	"	48.90	6.198	1.3257
38.31	"	48.50	6.148	1.3222

By plotting these results on a diagram two density curves are obtained cutting at 32.38° C, while the solubility curves cross one another at 32.37° C. The values thus obtained agree very closely with the transition temperature 32.379° C found by Richards and Churchill by the thermometric method.

A similar series of density determinations was carried out with manganous chloride, the tetrahydrate of which passes into the dihydrate at about 60° C. The following numbers were obtained:

Temp.	25°	30°	40°	50°	57.65°	60°	70°
Dens'y	1.4991	1.5049	1.5348	1.5744	1.6097	1.6108	1.6134

By plotting these results as above the value obtained for the transition temperature is about 59° C, whereas a dilatometric determination gave 57.9° C.

From the above it is evident that the determination of the density of the saturated solution may serve as an aid in the determination of transition temperatures. In the case of simple systems, such as we have made use of, the advantages of the method are not so obvious as for more complex systems where the equilibrium at the transition point is conditioned by saturation of the solution in respect to several salts and where an analytical determination of the composition of the saturated solution involves considerable time and analytical skill. Naturally the knowledge of the composition of the saturated solution permits a deeper insight into the equilibrium relationships along the various curves meeting in the multiple point, but in many cases this is not requisite.

The electrical conductivity method

As in the case of the density method, the applicability of this method was tested by the determination of the known transition temperature of Glauber's salt. Although many forms of apparatus for the determination of the electrical conductivity of solutions have been described, none of them are exactly suitable for the investigation of saturated solutions. For such determinations, especially at higher temperatures, it is essential that no opportunity be afforded for the solution to evaporate, and that the saturated solution may be transferred from the solubility vessel to the conductivity apparatus without any appreciable lowering of temperature, whereby crystallization of the solution is avoided. The higher the temperature the more easily will the accuracy of the determination be affected by these causes. In the experiments detailed below, the conductivity apparatus shown in Fig. 1 was used.

The apparatus consists essentially of two glass bulbs each of about 8 cc capacity, connected by a tube 2 cm long and about 2 mm internal diameter. A stout platinum wire fused into the glass at the outer end of each bulb carries a circular platinum plate serving as electrode. The outer ends of the platinum wires protrude into the tubes *a* and *b*, containing mercury, by means of which contact is made with the external circuit. The tubes *c* and *d*, opening into the lower and upper bulb respectively, serve to introduce the saturated solution. The tube *c* is attached by means of a rubber connection to the tube *e*, which passes through a double-bored rubber cork fitting into the solubility vessel. At its lower end this tube is provided with a small filtering arrangement filled with cotton wool. In making an experiment the stirrer was removed from the solubility vessel and, after allowing the suspended solid matter to settle, the rubber cork supporting the tube *e*, to which the conductivity apparatus was attached as described, was introduced as shown in the figure. The entire apparatus was then immersed below the surface of the water in the thermostat, so that only the upper ends of the tubes protruded. After an interval of some minutes to allow the immersed parts assuming the temperature of the bath, the saturated solution was drawn over into the conductivity apparatus by applying suction at *b* or pressure at *f*. By means of the clip shown in the figure, the apparatus could be kept full of the solution.

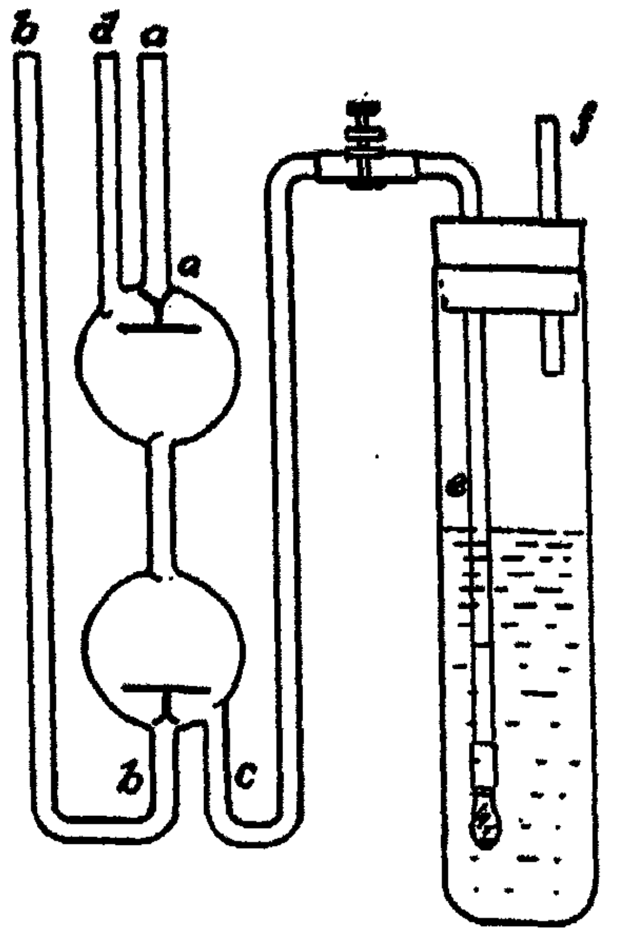

Fig. 1

The conductivity measurements were made in the usual manner; after each determination the saturated solution could be forced back into the solubility tube and a fresh saturated solution prepared at another temperature. The electrodes were platinized by means of the Kurlbaum-Lummer solution, and by special experiments we convinced ourselves that by making use of this solution for platinizing the electrodes, the size of the electrodes could be reduced to about ½ sq cm without any appreciable alteration in the sharpness of the tone minimum. A reduction of the size of the electrodes permits of the apparatus being made considerably smaller, and thus enables smaller quantities of saturated solution to be examined. The capacity of the apparatus was determined from a measurement of the conductivity of normal sodium chloride solution, the specific conductivity of which at 18° C is 919 × 10^{-8}.

The following numbers were obtained for saturated solutions of Glauber's salt and anhydrous sodium sulphate.

Temperature	Saturated solution of	Resistance Ohms	Specific conductivity
25.55°	Glauber's salt	318.5	1157 × 10^{-8}
27.00	"	303.6	1214 "
27.97	"	291.7	1264 "
29.15	"	282.2	1305 "
30.98	"	273.1	1349 "
31.22	"	271.1	1359 "
32.10	"	268.5	1372 "
33.23	"	265.9	1386 "
32.24	Anhydrous Na_2SO_4	269.5	1367 "
33.23	"	262.3	1405 "
33.83	"	258.6	1425 "
34.93	"	251.5	1465 "
36.87	"	239.5	1531 "
39.70	"	223.0	1652 "

If these numbers be plotted on a diagram in which the abscissa is taken as an axis of temperature and the ordinate as conductivity axis, the curves in Fig. 2 are obtained. The two curves indicate clearly some change in the system at about 32.5° C, corresponding to the transformation of Glauber's salt into anhydrous sodium sulphate. Obviously the change in direction of the conductivity-temperature at the transition temperature is not very considerable, and in view of the great change of the temperature coefficient of the solubility, a more decided change in the case of the electric conductivity was expected.

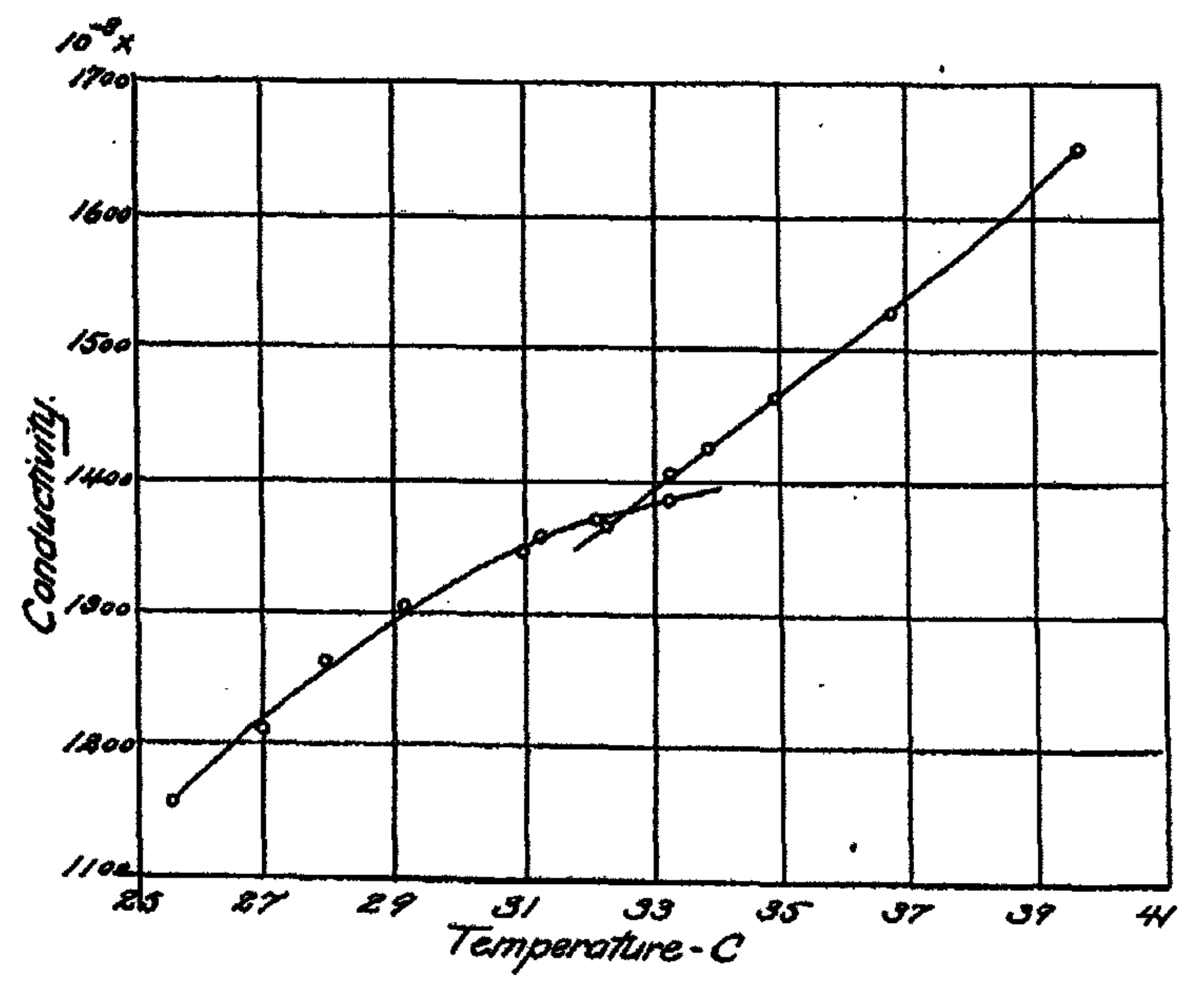

Fig. 2

This was moreover to be expected from the determinations of the electromotive force of the concentration chain formed by saturated solutions of sodium sulphate and a solution of sodium sulphate of constant composition by Cohen and Bredig. The electric transition cell in which these experiments were carried out was constituted as follows:

Reversible electrode	Sodium sulphate solution of constant strength	Saturated solution of the stable strength	Reversible electrode

To show the sharpness in the change of the temperature coefficient, the following numbers obtained for a normal solution of the salt are given:

Temp.	20.3° C	25.4°	30.3°	35°	40°	45.1°	
E. M. F.	7.2	11.2	16.7	22.2	22.4	22.9	millivolts

There is, however, an essential difference in the electromotive force method and the conductivity method. In the former case it is only the variation in concentration of a special ion which is the determining influence ; in so far as the electromotive force of the chain is concerned, the concentration of the other ions present or of the undissociated molecules in the saturated solution may vary without having any appreciable effect.

The determination of the conductivity does not however 'sample' the ions in this way; all the ions, simple or complex, take part in the conduction, and since in the concentrated solutions of sodium sulphate which come here into question, the concentration of the complex ion $\overline{NaSO_4}$ is no doubt considerable, the smallness in the change of temperature coefficient as compared with that for the difference of potential can be easily explained.

The essential cause of the small change observed is then, that while at small concentrations the specific conductivity of a salt solution increases rapidly with increasing concentration, in the case of moderately concentrated solutions changes of strength are usually accompanied by but small alterations in the specific conductivity. The following numbers show this sufficiently; as is evident even at moderate strengths increase of concentration is often accompanied by a decrease of conductivity.

Solution	Temperature	Specific conductivity
15% $MgSO_4$	15° C	4500×10^{-9}
20% "	15° C	4460×10^{-9}
25% "	15° C	3890×10^{-9}
20% K_2CO_3	15° C	1693×10^{-8}
30% "	15° C	2882×10^{-8}
40% "	15° C	2031×10^{-8}
20% $CaCl_2$	18° C	1616×10^{-8}
25% "	18° C	1665×10^{-8}
30% "	18° C	1550×10^{-8}

In order to ascertain whether this temperature coefficient shows a greater change in the case of systems where the concentration of the solution at the transition point is not nearly so great, a series of determinations was undertaken for thorium sulphate. Roozeboom has investigated the hydrates of thorium sulphate very thoroughly in regard to their conditions of equilibrium in contact with solutions of the sulphate. At the ordinary temperature the hydrate $Th(SO_4)_2.9H_2O$ is the stable form; at 43° C this undergoes decomposition, water being split off with formation of a tetrahydrate and saturated solution. Other hydrates are capable of existence, but these represent unstable forms at all investigated temperatures.

The solubility curves of the two above-mentioned hydrates cross each other at 43° at a very wide angle, and in consequence of the inertia of the hydrates as regards their capacity of transformation, Roozeboom was able to investigate the solubility of the nona-hydrate up to 50° C, and that of the tetrahydrate down to ordinary temperatures.

Since the concentration of the saturated solution of the sulphate at the transition temperature is only about one-third normal, the above-mentioned property is fairly well satisfied.

The thorium sulphate used in the experiments was purified by repeated crystallization of the nona-hydrate from water at ordinary temperatures. In the following table the values obtained for the resistance of the solution are given directly, the capacity of the apparatus used not having been determined.

Temperature	Saturated solution of	Measured resistance Ohms
25.05° C	$Th(SO_4)_2.9H_2O$	2237
35.02	"	1850
40.00	"	1568
44.90	"	1303
49.8	"	1067
45.05	$Th(SO_4)_2.4H_2O$	1114
52.2	"	1175
60.35	"	1226

If these numbers are plotted on a diagram with the abscissæ as temperature axis and the resistance as ordinate, the two curves shown in Fig. 3 are obtained; the two branches intersect at a point corresponding to 48° C. The change of direction at this temperature is very considerable, and indicates in a striking manner some change in the system at 48° C. Some later determinations of the conductivity of thorium sulphate solutions at higher temperatures indicate that the salt undergoes a gradual hydrolytic decomposition, the rate of hydrolysis increasing with the temperature. In consequence of this the conductivity of the saturated solution slowly increases at one and the same temperature, and the solution acquires an acid reaction. In the above series of experiments the influence of this hydrolysis was reduced as far as possible to a minimum by carrying out the determinations as rapidly as was concordant with the attainment of saturation.

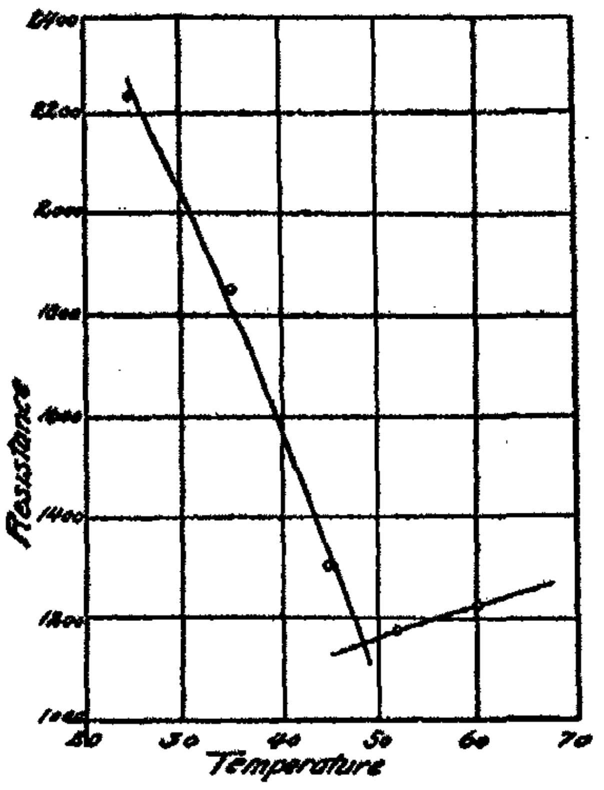

Fig. 3

When the result obtained by the conductivity method is compared with the transition temperature at 43° C found by Roozeboom, we find a difference of 5° C. This is too large to be accounted for by the difference in the method of determination, and in order to confirm if possible the value found by the electrical method, the transition temperature was determined by the dilatometric method and further by the vapor-pressure method.

About 5 grams of the hydrate $Th(SO_4)_2.9H_2O$ were brought into a dilatometer, which was then evacuated and filled with petroleum. After heating to about 65° to effect a partial transformation into the lower hydrate, the following observations were made:

Temperature	Level of petroleum in capillary
44.8° C	Fell 11 mm in 15 hours
46.8° C	Rose 0.4 mm in 18 hours
47.8° C	Rose 3.5 mm in 23.5 hours
45.8° C	Fell 2.8 mm in 27.5 hours

From these numbers it is evident that the transition temperature in question as determined by the change in volume of the system, is about 46.5° C.

The tensimetric method depends upon the equality of the vapor-pressures of the dry hydrate and of its saturated solution at the transition temperature. Three grams of the partially dehydrated nona-hydrate was introduced into one bulb of a Bremer-Frowein tensimeter and the same quantity of the moistened hydrate into the other. To serve as index, mercury was introduced, and after being evacuated the apparatus was heated in a thermostat, the temperature of which was regulated to 1/10° C, and the following observations taken:

Temperature	Difference of pressure
39.8° C	5.75 mm Hg (constant after 3 days)
44.8° C	2.7 " " " " 2 "
47.8° C	0.0 " " " " 4 "

From this determination the temperature at which the higher hydrate is transformed into the tetrahydrate lies between 47° and 48° C. The values thus obtained by means of the dilatometer and tensimeter agree sufficiently with the temperature determined from the variation of conductivity as to justify the applicability of the latter method to such transition point determinations, and to show that the temperature 43° C obtained by Roozeboom by the solubility method is somewhat too low.

In the above experiments the variation of the electrical conductivity has only been applied to the determination of transition temperatures in the case of simple systems composed of but two bodies. The advantages of the method will be however much greater in the case of a more complex system, where the analysis of the saturated solution is an operation requiring considerable time. The dilatometric and tensimetric methods have in such cases proved to be of great assistance in fixing the transition temperature, especially at higher temperatures. At lower temperatures, however, the facility with which many systems can exist in an unstable condition for considerable periods and the very small velocity with which the one system is transformed into the other (stable) form, even at temperatures considerably removed from the transition temperature, make the dilatometric determination somewhat difficult. Since, furthermore, the absolute values of the vapor-pressure of chemical systems at lower temperatures are small, the tensimetric method fails also in this case. In such cases the electric conductivity will no doubt be a valuable aid in determining the existence of a transition temperature. Experiments are being made on the application of conductivity measurements to the study of double salt formation.

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THE DRIVING TENDENCY OF PHYSICO-CHEMICAL REACTION, AND ITS TEMPERATURE COEFFICIENT[1]

BY THEODORE WILLIAM RICHARDS

Every beginner in physical chemistry of course notices the similarity in form of the equations of Clausius and van 't Hoff,

$$\frac{d\,ln\,P}{dT} = \frac{\lambda}{RT^2} \text{ and } \frac{d\,ln\,K}{dT} = \frac{U}{RT^2}.$$

The differences in the interpretation of the signs are the only hindrance to the welding of the two equations into one. P usually consists of a single quantity, a pressure, while K is usually a product of concentrations. On the other hand, the second member of the equation sometimes includes work ($\lambda = -U + A$) and sometimes means simply the diminution of the internal energy, or the heat given out, in a process conducted at constant volume (U).

Since these distinctions are so confusing that errors from the lack of proper discrimination have crept into some of our most valuable treatises, the present paper, which is a treatment of the subject from a single point of view, may be of interest. I have found it advantageous, both in teaching and in thinking, to look at the whole field from the point of view of *pressure.* This practice has recently received support in an interesting article by Arrhenius[2] on the speed of reactions.

That the pressures affecting a given reaction should exert the deciding influence in determining the magnitude and direction of a chemical change, is no more astounding than that the

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[1] Simultaneously published in Proc. Am. Acad. 1900.

[2] Zeit. phys. Chem. 28, 317 (1899).

resultant of mechanical forces should be the agent determining the change of position of finite masses. Pressure seems to be therefore a more direct point of attack than either volume, concentration, or entropy, in the analytical study of physico-chemical reaction.

There are of course many possible ways of attacking the subject mathematically. Perhaps the simplest is given below. In his recent comprehensive and interesting paper on equilibrium and free energy, Lewis[1] has shown that the following equation, that of van 't Hoff, is a general one, applying to both homogeneous and heterogeneous systems, but rigorously accurate only when the system is composed of ideal gases, dilute solutions and "condensed" phases of constant volume.

$$\frac{d}{dT} ln \frac{v_2^{n_2} v_2'^{n_2'} \ldots}{v_1^{n_1} v_1'^{n_1'} \ldots} = \frac{d}{dT} ln \frac{c_1^{n_1} c_1'^{n_1'} \ldots}{c_2^{n_2} c_2'^{n_2'} \ldots} = \frac{U}{RT^2}.$$

In this expression v means molecular volume; T absolute temperature; c concentration $\left(\frac{1}{v}\right)$; n the number of reacting molecules of any given molecular species; U diminution in the internal energy of the process, or the heat of reaction at constant volume; and R the gas constant (1.98 cal. units, or better 8.31 c. g. s.). The products of a reaction are indicated by a subscript 2, the factors by 1. The chief disadvantage of the equation for practical purposes is the fact that the numerator in the second member does not always represent the actual heat of the reaction.

Let us now introduce pressure instead of concentration into this expression. $c = \frac{p}{RT}$; hence the expression becomes

$$\frac{d}{dT} ln \frac{(RT)^{(n_2 + n_2' \ldots)} p_1^{n_1} p_1'^{n_1'} \ldots}{(RT)^{(n_1 + n_1' \ldots)} p_2^{n_2} p_2'^{n_2'} \ldots} = \frac{U}{RT^2}.$$

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[1] I am much indebted to Dr. Lewis for valuable mathematical criticism of the present paper. To Drs. Hall and Buckingham also I owe thanks for interest and suggestions as to matters of detail. Since reading the manuscript the latter has derived the "reaction isobar" according to the method of Duhem, but in the present exposition I have retained the original derivation according to the notation of Nernst, because this notation is more familiar to most physical chemists.

Cancelling the unnecessary powers of RT, we have

$$\frac{d}{dT} ln \frac{RT^{(n_2 + n_2' - n_1 - n_1' \dots)} p_1^{n_1} p_1'^{n_1'}}{p_2^{n_2} p_2'^{n_2'}} = \frac{U}{RT^2}. \qquad (2)$$

Let us consider for the sake of argument a case in which $(n_2 + n_2' \dots - n_1 - n_1') = N$ is positive; that is, a case in which the total number of gram-molecules in the product is larger than that in the reacting mixture before the reaction took place. The expression then becomes

$$\frac{d}{dT} ln \frac{(RT)^N p_1^{n_1} p_1'^{n_1'}}{p_2^{n_2} p_2'^{n_2'}} = \frac{U}{RT^2}. \qquad (3)$$

The numerator of the second term of this modified equation of van't Hoff still consists merely of U; hence if the equation is to be used with data obtained under constant pressure, the observed heat of reaction must be corrected for the work done during expansion. For this reason its prototype has been called the "reaction isochor" by Nernst; it represents immediately the observed conditions only when the reaction takes place in a constant volume. The introduction of the correction causes an interesting simplification.

At constant pressure the observed evolution of heat during the reaction would be less than U, because the work NRT is done against a constant pressure; hence we must subtract $\frac{NRT}{RT^2} = \frac{N}{T}$, from each side of the equation, in order that the numerator of the second member of the equation should truly represent the observed conditions.

Since $\frac{N}{T} = \frac{N\,d\,ln\,T}{dT}$ and $d\,ln\,R = 0$, by subtracting the equations we obtain

$$\frac{d}{dT} ln \frac{p_1^{n_1} p_1'^{n_1'} \dots T^N}{p_2^{n_2} p_2'^{n_2'} \dots} - \frac{N\,d\,ln\,T}{dT} = \frac{U}{RT^2} - \frac{NRT}{RT^2}.$$

Simplifying, and noting that $U - NRT = -\lambda$, the heat actually evolved in the reaction, we may write

$$\frac{d}{dT} ln \frac{p_1^{n_1'} p_1'^{n_1'} \dots}{p_2^{n_2'} p_2'^{n_2'} \dots} = -\frac{\lambda}{RT^2}. \qquad (4)$$

Here λ represents the actual absorption of heat when the reaction takes place under constant gas or osmotic pressure. The equation holds true under either constant volume or constant pressure; but only in the latter case does the second member represent the observed heat of reaction.

Hence at constant outside pressure the heat observed in any reaction bears a very simple relation to the acting pressures which take part in that reaction, just as at constant volume the concentrations are similarly related to the observed evolution of heat. This equation (4) may be called the "Reaction-isobar," on account of the fact that it is peculiarly applicable to reaction which takes place under constancy of total pressure. The equation of Clausius is a special case of this law. Clearly this equation provides a much more convenient basis for the calculation of data obtained under constant pressure, than the old concentration equation. It applies especially to reactions between gases, because here the reaction often takes place under constant pressure.

Returning to the pressure equation at constant volume, from which we omit $d\,ln\,R^N$, we have

$$\frac{d}{dT}\,ln\,\frac{p_1^{n_1}\,p_1'^{\,n_1'}\dots T^N}{p_2^{n_2}\,p_2'^{\,n_2'}\dots} = \frac{U}{RT^2}. \qquad (5)$$

As usual, the second member indicates the heat actually evolved.

Here two cases may arise. If $N = 0$, that is, if the osmotic or gas pressure (or total number of molecules) does not change during the reaction, the pressure remains constant. Mathematically, T^N becomes 1 and hence disappears; the equation depicts the reaction-isobar doing no outside work. On the other hand, if $N \gtrless 0$, T^N becomes a serious factor in the equation, affecting immensely the temperature coefficient of the "Mass-law constant."

In any case, since equation (5) is restricted to constant volume by the presence of U alone in the second member (which is understood to signify that heat actually evolved), it may properly be called a "Reaction-isochor."

Evidently the reactions-isobar and isochor may now be combined into one, for the obstacles to this union are removed. Before combining them it is advantageous to examine into the meaning of $d\,ln(\mathrm{RT})^{\mathrm{N}} = d\,ln\,\mathrm{T}^{\mathrm{N}}$, which constitutes the only puzzling difference between them.

The physical meaning of this important factor in the equation is interesting. From its mode of introduction into equation (2) this term is clearly the representative of the pressure caused by an addition to the total number of molecules in a given space. When the total pressure is artificially maintained at a constant value, $ln\,\mathrm{T}^{\mathrm{N}}$ disappears from the equation just as it does when the pressure remains constant because the total number of molecules present is not increased by the reaction. This is equivalent to defining N in its present situation as a direct function of the *increase of the total pressure of the reacting substances* during the reaction. In order to avoid conflict with the original definition of N, we shall call this newly defined exponent N′. Mathematically, the inspection of equations (4) and (5) shows that the expression $\mathrm{N}' = \mathfrak{M}\frac{\mathrm{P}_2 - \mathrm{P}_1}{\mathrm{P}_1}$, (where $\mathfrak{M}$ is the total number of gram-molecules in the initial reacting mixture, and P_1 and P_2 the initial and final total pressures respectively), is true either for constant pressure or constant volume. Whether this still holds true for the ill-defined cases where neither volume nor pressure is constant, we shall not at present determine. In constant volume, according to this definition, $\mathrm{N}' = \mathrm{N}$; under constant pressure, likewise according to this definition, $\mathrm{N}' = 0$.

With the help of this new definition, together with the use of the symbol $-\mathrm{Q}$, to signify the heat actually evolved in the reaction, it becomes possible to combine the reactions-isochor and isobar into one equation, from which either may be logically obtained again, according to the circumstances attending the reaction. Thus we may write

$$\frac{d}{d\mathrm{T}}\,ln\,\frac{p_1^{n_1}\,p_1'^{n_1'}\ldots\mathrm{T}^{\mathrm{N}'}}{p_2^{n_2}\,p_2'^{n_2'}\ldots} = -\,\frac{\mathrm{Q}}{\mathrm{RT}}. \qquad (6)$$

If the total osmotic or gas pressure is kept constant, $\mathrm{N}' = 0$, no matter what N may be, hence $T^{N'} = 1$ and disappears, and $Q = \lambda = NRT - U$. This is the reaction-isobar. If on the other hand, the *volume* is kept constant, $T^{N'}$ corresponds to the increase of pressure, which under constant pressure would have represented work, and $-Q = U$. This is the reaction-isochor. If both $N = O$ and $-Q = U$, the equation is both isochor and isobar. Equation (6) is then a general expression for the temperature coefficient of the equilibrium ratio[1] of dilute or ideal reactions.

For this general expression, I propose the name "reaction-metatherm" (μετά, between). The chief practical advantage, which it possesses over the usual concentration equation is the fact that its second member contains always the heat actually evolved, whether work is done or not.

Since this is the case, the expression must be an analytical statement of the theorem of Maupertuis or Le Chatelier, as far as heat is concerned. In order to trace this evident necessity, one must assume a somewhat puzzling inverted attitude. The pressures indicated by the formula define a condition of equilibrium, not a condition of action. It is clear, then, that a small pressure in the numerator of the logarithmic expression means a great tendency towards the denominator. That is, a growing denominator means an increasing tendency to change from factors to products. When the logarithms in the denominator grow faster than those in the numerator, the minus sign of the second member is cancelled. Hence a reaction which absorbs heat evidently must be pushed farther by increasing temperature.

This is of course not a statement of the incorrect "law of maximum work"—it concerns merely the *change* in the tendency of the reaction with the heat, and does not imply that a reaction which absorbs heat will never take place. The equation represents merely the *variable* tendencies.

The inverted attitude already mentioned may be easily remedied by considering carefully the nature of the quantities

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[1] This satisfactory name is due to Lewis. "Mass-law constant" is a less satisfactory name because the ratio is not constant, and the law is probably not a mass law.

involved. We have seen that the expression $ln \frac{p_1^{n_1} \ldots}{p_2^{n_2} \ldots} = k$ (the familiar "mass-law" expression for equilibrium expressed in terms of pressure), seems to represent the resultant reacting tendency of a given reaction at constant temperature; because it is this quantity which is concerned with the theorem of LeChatelier. When concentrations are used, it is difficult to imagine any physical meaning in this equilibrium ratio; but when the expression is conceived of in terms of pressure, we may look upon k as a similar opposing pressure tendency just equal to the ratio of the pressures actually observed. That is to say, we may call k the "reaction tendency" or "driving tendency" of the reaction.

We may conceive of this reaction-tendency as consisting of a number of individual reacting tendencies, one for each substance. But the pressures in the pressure-equilibrium ratio, do not directly represent the individual reacting tendencies of the substances represented. They are only the pressures which remain in equilibrium when all the reacting forces have been balanced. When under these circumstances a given individual pressure is small, we must ascribe to that substance a great reacting tendency, and vice versa. Thus it seems to me probable that each of these pressures must have a term in the function k, which corresponds to its tendency to react, and this individual tendency shall be called $ln\, z$, a term which will be in the numerator when the corresponding pressure is in the denominator, and vice versa. The reasoning may be stated in the form of an equation:

$$ln \frac{p_1^{n_1} p_1'^{n_1'} \ldots}{p_2^{n_2} p_2'^{n_2'} \ldots} = ln \frac{z_2^{n_2} z_2'^{n_2'} \ldots}{z_1^{n_1} z_1'^{n_1'} \ldots} .$$

This equation is simply a definition of the value z, which is made logarithmic from analogy to the other pressures.

One must bear in mind, however, that an individual z, or single "physico-chemical potential" need not be the *reciprocal* of p; for the condition of equilibrium demands only that the *total sum of the logarithms* on each side must be equal, and not that the individual opposites are immediate functions of one another. The p values depend of course upon the amount of substance present, while the z values are constant for any given temperature, because they are by definition the constant factors which build up a constant. Any constant tendencies, not given by the differential equation, may hence be included among the z values.

Transposing the second member, we obtain

$$ln\,\frac{p_1^{n_1}p_1'^{n_1'}\ldots z_1^{n_1}z_1'^{n_1'}\ldots}{p_2^{n_2}p_2'^{n_2'}\ldots z_2^{n_2}z_2'^{n_2'}\ldots}=0. \tag{7}$$

This expression may be written

$$n_1\,ln(p_1z_1)+n_1'ln(p_1'z_1')\ldots-n_2\,ln(p_2z_2)-n_2'ln(p_2'z_2')\ldots=0.$$

Except for its logarithmic form and the substitution of pressure for mass, this equation reminds one of Berthollet's old statement concerning chemical action. It is a fundamental equation of chemical equilibrium in dilute or ideal mixtures.

Stated in words, the equation reads: each molecule taking part in a reaction may be said to possess at any given temperature a reacting tendency which is the logarithm of the product of its constant physico-chemical potential and variable observed pressure. Obviously the logarithmic arrangement is so convenient as almost to demand its adoption,—although the same idea might have been expressed otherwise. One may say, for example, that in equilibrium the algebraic sum of the opposing tendencies concerned is zero—almost an axiom. The logarithmic equation is a plausible hypothesis, which is concordant with many other natural tendencies.

The substitution of this value instead of its pressure equivalent in the equation gives us a less inverted view of the theorem of Le Chatelier.

$$\frac{d}{dT}\,ln\,\frac{z_2^{n_2}z_2'^{n_2'}\ldots T^N}{z_1^{n_1}z_1'^{n_1'}\ldots}=\frac{-Q}{RT^2}.$$

It will be seen at once that the reacting tendencies of the initial substances, z_1, z_1', etc., agree in sign with Q; that is, a reaction which absorbs heat will have a greater tendency to take place as the temperature rises.

The only immediately obvious advantage of the dissection of the k value is this interpretation of the sign of the second member of the reaction metatherm. It seems to me, however, that the idea is capable of expansion and of wide application, because it brings unknown individual chemical tendencies under the same method of treatment as well known physical ones. These reacting tendencies probably express the chemical potentials demanded by the Phase Rule of Willard Gibbs, and the new point of view may afford opportunity for the numerical study of them.

Just as we may look upon the vapor tension of a liquid as the resultant of the physical attractive and disruptive forces at work on the surface, so we may look upon this $\ln z$ as being the resultant of similar chemical attractive and disruptive forces at the surfaces of the smallest particles, a resultant which must be perfectly definite in a definite environment. Further treatment of this matter must be reserved for a subsequent paper.

Since the original equation from which the reaction metatherm was derived holds true for ideal heterogeneous as well as for homogeneous equilibrium, we may introduce phase-pressures, such as vapor or solution tensions, into the pressure equations. These phase-pressures resemble the z values, in many ways; they will be designated by P below, in accordance with the usual custom.

It is perhaps worth while to give a few examples of the application of the pressure equations, in order to show especially that the sign of Q is always correctly indicated, and hence that no confusion arose in the derivation of the equations. These examples simply show the reappearance of the principles underlying the whole treatment; they furnish no unexpected result, but their easy unravelling shows the convenience of treating the matter from a single point of view.

For example, in the case of an evaporating liquid, we may say that the force concerned is the vapor-tension, which therefore takes the place of z_1. There are no opposing forces except the walls of the vessels and the gas-pressure, which is simply a carrier; hence the equilibrium equation becomes $ln\frac{k}{P} = 0$—an obvious truth; and the equation metatherm reduces at once to the equation of Clausius.

Again, let us consider the evaporation of water from a crystallized salt, where the treatment is equally simple. The water has a certain reacting tendency or driving energy, which manifests itself as a definite pressure at each temperature. Precisely the same explanation applies to calcic carbonate, or any other similar case.

A more complicated case is the evaporation of ammonic sulphydrate. Here we have to consider the physical reacting tendency of the evaporating substance, which is balanced by the pressure of the ammonic sulphydrate, as well as the physico-chemical potentials and actual pressures of the three molecular species. The equation of equilibrium would then be

$$ln\frac{p_1(p_2z_2)^{NH_3}(p_2'z_2')^{H_2S}k}{P(p_1z_1)^{NH_4SH}} = 0.$$

This expression is an analysis of the forces which are at work in maintaining equilibrium. p_1, the pressure of the undissociated NH_4SH, occurs first in the numerator as opposing P, the sublimation tension of the solid substance, and then in the denominator as a factor of the chemical reacting tendency of the ammonic sulphydrate. These two of course cancel; and since at constant temperatures all the z values are constant, we obtain for the chemical part of the equilibrium the familiar expression

$$p_2p_2' = k_1.$$

This is entirely in accord with the results of Isambert, and is undoubtedly true.

Many other examples of the application of the pressure equations might be given. For example, the dissociation of nitric peroxide is easily treated by the reaction-isobar, while that of hydrobromic acid needs merely the simplest form of all, which is both isochor and isobar. Moreover, it is obvious that upon introducing electrolytic solution tensions and osmotic pressures into the reaction isobar, it becomes at once the familiar Nernst-Helmholtz expression for the temperature coefficient of electromotive force. In short, whenever pressures are under consideration, the reaction metatherm affords a ready means of treatment.

The results of this paper may be summarized as follows:

1. It is pointed out that the study of pressure affords a more direct method of analyzing the progress of a reaction than in the study of volume, concentration, or entropy.

2. An expression called the "reaction metatherm" has been evolved which represents in terms of pressure the temperature coefficient of the equilibrium ratio of physico-chemical reaction.

3. Since this equation always has as its second member the heat actually evolved in the reaction, whether under constant volume or constant pressure, it is a mathematical expression of the theorem of Maupertuis or Le Chatelier.

4. Moreover, since the equation represents this fundamental theorem, its logarithmic quantity must represent the variables in the reacting tendency, or the driving energy of reaction.

5. When analyzed, this equation shows that the part played by each substance in a reaction may be considered as the logarithm of the product of its "physico-chemical potential" and its actually present pressure.

6. The reaction-metatherm may be simplified into a reaction-isobar and a reaction-isochor, according as the pressure or volume is kept constant during the reaction.

7. While the reaction-isobar, expressed in terms of pressure, offers the most convenient basis for calculation from data obtained under constant pressure, results obtained under constant volume are more conveniently calculated if the reacting substances are expressed in terms of concentration, according to the equation of van 't Hoff.

Harvard University,
April 3, 1900

NEW BOOKS

Mesure des Températures élevées. *By H. Le Chatelier et O. Boudouard.* (*Bibliothèque de la Revue générale des Sciences*). *14 × 22 cm; pp. 220. Paris: Georges Carré et C. Naud, 1900. Price: cloth, 5 francs.*—Pyrometry, which was formerly a mere comparison of different available temperature functions, is now ripening into a science of considerable rigor, in proportion as the air thermometry of high temperatures is being more fully mastered. The errors at 1000° will not exceed 10° on the absolute scale, though at 1500° they may run as high as 50°. In the very readable book before us, Le Chatelier and his assistant have given a terse and practical account of the subject, which, from the broad pyrometric experience of the former, is obviously trustworthy throughout. The introductory chapters contain a selection of standard data, a discussion of the meaning of absolute temperature, a description of the normal (hydrogen) air thermometer at the *Bureau International*, an enumeration of the errors incident to high temperature air thermometry, and like matter, all very useful and well digested. Nothing is said, however, of the remarkable work which Holborn and Day are doing at the *Reichsanstalt*, nor of their great find that the platinum-iridium alloy is impervious to nitrogen (the best of pyrometric gases), and rigid at the highest temperatures. Under displacement air thermometry there is a similar lapse, seeing that it is left without reference to Victor Meyer, who is the virtual creator of the subject in its modern aspects. It seems inexcusable in a chemist to overlook the "*Pyrochemische Untersuchungen*," with their abundance of information on molecular stability at high temperatures. The remarkable interferential pyrometer due to D. Berthelot, (paired beams of light passing through tubes of like low density, the decrement being produced in one case by low pressure, in the other by high temperature), together with other new apparatus, is fully described.

In calorimetric pyrometry (Le Chatelier gives diagrams of serviceable apparatus). Nickel has recently been substituted for anomalous iron and expensive platinum.

Callendar and Griffiths's perfected Siemens pyrometer, now the most accurate of instruments for temperatures ranging below 1000° almost as far down as the absolute zero of temperature, is conscientiously described, and a long chapter, with details as to couples, galvanometers, furnaces, crucibles, is naturally devoted to thermoelectric pyrometry, in which Le Chatelier himself has been so usefully interested.

The discussion of radiation pyrometry is inadequate in so far as it contains no inkling of the labors of Wien, Lummer, Planck, and others who are successfully recasting the subject. To photometric radiation pyrometry much space is given. The final chapter on Seeger's cones (earthy mixtures of known fusing or sagging points), may be of interest to chemists, though these cones are now obtainable in the market.

The book will be a faithful mentor to anybody interested in pyrochemistry; and since Nernst has discovered that at high temperatures all earths are electrolytic conductors of a peculiar kind (of a kind in which there is certainly electrolysis with either anion or cation apparent), a field of great chemical importance is likely to be opened in this direction. *C. Barus*

Vorlesungen über hydrodynamische Fernkräfte, nach C. A. Bjerknes' Theorie. *By V. Bjerknes. Band I. 17 × 26 cm; pp. xvi + 338. Leipzig: Johann Ambrosius Barth, 1900. Price: paper, 10 marks.* — Among the attempts to explain the nature of force in terms of the medium through which it acts, those based on the hydrodynamics of an incompressible, frictionless fluid seem most at hand, inasmuch as the inevitable ether is given as such a fluid at the outset. The irrotationally moving fluid surrounding a vortex has been used as a field of this kind by Kelvin; and J. J. Thomson has shown at length, that whereas stable groups of aggregated vortices are possible up to eight in number, beyond this all grouping becomes unstable, thus suggesting close relations to atomicity. The technical difficulties in the way of the vortex hypothesis have barred its progress. On the other hand, the vibratory and pulsating theory, which had an independent origin throughout and need not be incompatible with the former, has now many achievements in its favor. That force can be derived from the impact of a wave train is evidenced by the radiometer, but the mechanism of this apparatus is too complex to be suitable. Kelvin showed that waves lash the boundary of the medium with a pressure per square centimeter equal to the product of half the density of the medium and the square of the wave velocity. Mayer's famous experiment with pivoted resonators rotating in the acoustic field of their own notes was shortly after its discovery explained by Rayleigh, proving that the internal pressure in a resonator exceeds atmospheric pressure, so that a force exists at the mouth directed normally inward.

Long before all this, before Faraday had proclaimed his doctrine of lines of force, and before Maxwell had developed that doctrine, indeed almost before Kelvin had published his method for the solution of hydrodynamic problems by Hamilton's principle, the elder Bjerknes had independently become dissatisfied with "action at a distance", and had tentatively suggested a remedy. As far back as 1868 (Maxwell's great treatise was completed in 1873), with the simplest of media (frictionless, incompressible fluid), and the geometrically simplest solid (a sphere), Bjerknes had found that the force actuating the center of one of two spheres and arising in a second moving sphere, has the same intensity and direction as if the former were absent, and is equal to the acceleration in question multiplied by 3/2 of the medium displaced by the first sphere — certainly a suggestive proposition, though it did not then predict Newton's third law. Meanwhile Kirchhoff had adopted Kelvin's hydrodynamic method, and had developed it for problems of precisely the present kind, with his usual ability. Bjerknes was then able to apply the Kelvin-Kirchhoff investigation to his own researches with such success as not only to deduce the law of action and reaction as a necessary property of his own mechanism, but to show that pulsating spheres act on each other through the medium by stressing it into a field of force *mutatis mutandis* identical in character with the action on each other of magnetic or electrical molecules.

These papers have been much sought after by physicists, in spite of their inaccessibility and the fact that demonstrations were often withheld. It is therefore fortunate that the younger Bjerknes, an equally able investigator, has collected the work of his father in a systematic treatise, of which the first volume is now before us. As above indicated, the book treats at length of the motion (vibration, translation) of a system of spheres of variable (pulsating) volume) submerged in the ideal fluid stated, preliminarily to deriving action at a distance from purely hydrodynamic phenomena. The book is therefore not without interest to the chemist, for the behavior of molecules imbedded in ether is precisely such as falls within the scope of Bjerknes's investigation.

It would be going too far to examine the work in detail, and such an examination, without mathematics, would be most unsatisfactory. Investigations like the present are usually made by deriving the particular equations of motion, and then so transforming them that they may be identical in character with those of the known phenomenon which it is aimed to explain. The remainder of the work is an interpretation of corresponding terms, parameters, and constants. Suffice it to add, therefore, that in 1878 Bjerknes investigated the condition of rotational stability of the axis of permanent oscillation of spheres in an oscillating medium, and found both a pulsating pair or a single oscillating sphere to be subject to torque, the final link in his argument.

A reexamination thus reveals that Newton's first, second, and third laws have all been deduced, inclusive, of course, of inertia. Hydrodynamic forces may be superposed, which is a predication of vector summation. They are independent of the velocity of the body actuated. The system admits of concealed motions (potential energy); it is subject to the law of the conservation of energy, and its potential to Laplace's equation. In a general way, hydrodynamic forces vary as the product of the volumes (ultimately masses) of mutually reacting spheres. Specifically, two identically pulsating spheres attract each other, two oppositely pulsating spheres repel each other, with a force varying as the density of the medium and the intensity of pulsation, and inversely as the square of their distance apart. Furthermore, action of magnetic character (attraction, repulsion, rotation) occurs between oscillating and pulsating systems. Finally, heavy spheres of opposed pulsations attract each other at long ranges and repel each other at short ranges, with a position of stable equilibrium for an intermediate range. The converse holds for spheres lighter than the medium.

It is hardly necessary to give further examples of the contents of this remarkable book. The author has been gracious in collecting the chief dynamic and hydrodynamic principles in the introduction, for the convenience of the reader, but a good working knowledge of applied mathematics is necessarily presupposed.

C. Barus

Vorlesungen über theoretische und physikalische Chemie. *Drittes Heft: Beziehungen zwischen Eigenschaften und Zusammensetzung. By J. H.*

van 't Hoff. 15 × 23 cm; pp. x + 136. Braunschweig: F. Vieweg und Sohn, 1900. — This third and last part of the work deals with the relations between properties and composition. The physical properties are first considered. We find a discussion of the gas laws, and of the modifications proposed by van der Waals and by Clausius, with special reference to corresponding states, relation between the critical and the theoretical volume, the theorem of the rectilinear diameter, and Berthelot's conclusions in regard to the density of liquids. The additive and constitutive volume relations are next considered, there are a few words on pressure phenomena, and then we come to temperature relations. Here we have the boiling-points of isomers and the change of the boiling-point with the molecular weight, with the nature of the substituting radicals, and with the molecular symmetry. The next section very naturally deals with latent heat of vaporization, and with the specific heats of solid, liquid, and gaseous elements and compounds. A fifth section treats of the relation between surface-tension and molecular weight, while the optical phenomena are discussed in the sixth section.

The relation between chemical properties and the composition is divided into two rather long chapters and one very short one. In the first we are shown that the properties of a compound stand in some relation to the properties of the composing elements; in the second, attention is drawn to the modification of the properties of an element by the nature of the other elements in the compounds, while the third chapter deals with such substances as the iodonium compounds where the properties are entirely abnormal. This is a very interesting and clever method of dividing the subject and one wishes that a final chapter had been added in which there could have been a discussion of the reasons why certain compounds come in one of the three classes rather than in either of the other two. Of course, these reasons are hinted at in the text, so far as they are known; but there are few things so conducive to progress as a clear succinct statement of what we do and do not know.

Wilder D. Bancroft

Analyse électrochimique. *By Edgar F. Smith. Translated from the Second, American, Edition, by Joseph Rosset. 12 × 19 cm; xvi + 203 pp. Paris: Gauthier-Villars, 1900. Price: paper, 3 francs.* — It is quite an encouraging sign to find an American textbook on electrochemical chemistry appearing in a French translation. The book is divided into three parts: apparatus and a brief historical sketch; determination of metals; separation of metals. In the second part, methods are given for determining copper, cadmium, mercury, bismuth, silver, zinc, nickel and cobalt, manganese, iron, uranium, thallium, platinum, palladium, rhodium, ruthenium, molybdenum, gold, tin, antimony, arsenic. In the third part, methods are given, so far as known, for separating any one of the preceding metals from any of the others.

In some respects the book is excellent; in others it is open to criticism. The literature references are full and data published last year by Miss Kollock have been included. In too many cases, however, the current is given in terms of the gas voltameter; the definitions of volt, ohm, and ampere (p. 7) are unsatisfactory from a theoretical and a practical point of view; the Weston ammeters are not mentioned, though they are much superior to the Kohlrausch instrument; the electromotive force of the Clark cell is not 1.457 volts. Although the book is intended merely as a laboratory manual, the reviewer would have liked to have seen a brief statement why two metals can be separated in one solution and not in another. For the benefit of the teacher, if not for that of the student, it would have been well to have indicated why the metals were taken up in one particular order, rather than in any other. These shortcomings may seem trifles to many; but "trifles make perfection, and perfection is no trifle."

Wilder D. Bancroft

Über freiwillige Oxydation. *Beiträge zur Kenntnis der Autoxydation und Sauerstoffaktivierung. By W. Manchot. 15 × 23 cm; pp. 48. Liepzig: Veit und Comp. 1900. Price: 1.50 marks.*—When oxanthranol in aqueous solution was oxidized by air, it was found that the ratio of hydrogen peroxid to decomposed oxanthranol was less than unity, and that the value was smaller, the slower the oxidation. Experiment showed that the oxanthranol was oxidized by the hydrogen peroxid. Addition of barium hydroxid eliminated this source of error, sparingly soluble barium peroxid being formed. Under these circumstances exactly one-half the oxygen is made active. The same result was obtained when dihydrophenanthrenequinone, hydrochrysoquinone, or hydroretenquinone was substituted for oxanthranol. The same ratio was obtained with two hydrazo compounds. Curiously enough, the author does not look upon these facts as confirming van 't Hoff's theory.

The pamphlet closes with a discussion of the effect of alkali upon autoxidation. This section is not developed in a very satisfactory manner and we are left with a confused impression of change of dissociation, hypothetical rate of oxidation of ions, and catalytic action of free alkali.

Wilder D. Bancroft

La Liquéfaction des Gaz et ses applications. *By Julien Lefèvre. (Encyclopédie scientifique des aide-mémoire). 12 × 19 cm; pp. 174. Paris: Gauthier-Villars. Price: paper, 2.50; boards, 3 francs.*—The arrangement is slightly different from that in the other works on the subject. There is first a short chapter on the general thermodynamic theory of gases, and this is followed by chapters on the liquefaction of gases; the reduction of the 'permanent' gases to static liquids; special investigations with acetylene, ozone, fluorin, argon, and helium; liquefaction of gases on a commercial scale; keeping liquefied gases and properties of the same; studies near the critical point; application of liquefied gases; freezing machines. The general impression is that the order of the chapters must have been determined by lot.

Wilder D. Bancroft

Leçons d'Optique géométrique. *A l'usage des Élèves de mathematiques spéciales. By E. Wallon. 16 × 25 cm; pp. 343. Paris: Gauthier-Villars, 1900. Price: paper, 9 francs.*—If the reader is desirous of perusing a rigorous and elegantly written treatise on geometric optics, he will do well to consult this book. The somewhat familiar works of Heath and of Parkinson are more abrupt. Having done so, however, if he expects to be familiar with the modern microscope, telescope, spectroscope, or the variously intricate photographic lenses, he will be unhappily disappointed. The setting given to Gauss's contributions, which revolutionized geometric optics, is out of proportion in its meagerness; and the (diffractive) work of Abbe, with its fundamental bearing on the modern practice of optical construction, lies beyond the scope of the book. All this is in strong contrast with the admirable work of Czapski, or of Strehl, for instance, men who bear in mind that whoever reads geometric optics nowadays is likely to do it for practical purposes. *C. Barus*

Modes opératoires des Essais du Commerce et de l'Industrie. *By L. Guniasse et R. Zwilling. Avec préface de Ch. Girard. 11 × 17 cm; viii + 302 pp. Paris: Georges Carré et C. Naud, 1900. Price: cloth, 6 francs.*— "Un traité que n'est ni trop élémentaire, ni trop savant, d'abord facile et pourtant précis, livre de classe et livre de laboratoire—tel me paraît être le manuel d'analyse de MM. L. Guniasse etR. Zwilling" from the preface de *Préface de M. Ch. Girard.*

Twelve pages are devoted to tables for the detection of acids and bases, six more to a list of the reactions of the commoner elements, and organic salts, arranged alphabetically, eight pages suffice to explain the principles of quantitative analysis, and the remainder of the book is divided into chapters on the technical analysis of waters, air, minerals, and inorganic preparation, sugar, petroleum, ore, rubber, dyestuff, milk, soap, textiles, vinegar, ales, spirits, urine, etc., etc.

In addition to the usual chemical and electrochemical operations, the use of the microscope, polariscope, lactoscope, ebulliscope, and various flash-point apparatus are described; as is also that of the "Dazymètre", a small testing machine for determining the tensile strength of paper.

The descriptions, though condensed, are clear and in most cases detailed enough; and the forty-eight figures are well drawn and clearly printed.

W. Lash Miller

Analyse chimique qualitative. *By M. E. Pozzi-Escot. (Encyclopédie scientifique des aide-mémoire). 12 × 19 cm; pp. 180. Paris: Gauthier-Villars. Price: paper, 2.50 francs.*—This is a condensed summary from the treatises of Carnot and of Ditte. It has the advantage over some of the briefer manuals that the rare earths are included. *Wilder D. Bancroft*

REVIEWS

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

General

On thermodynamics. *K. Wesendonck. Wied. Ann.* 67, *447* (*1899*). — The author states that people have overlooked or ignored the point made by Clausius, that the temperature to be considered in the change of the entropy is the temperature at the surface of the body passing through the cycle. The temperature of the reservoirs has nothing to do with the case. The bearings of this on recent work is discussed.

W. D. B.

On the thermokinetic properties of solutions. *L. Natanson. Zeit. phys. Chem.* 30, *681* (*1899*). — An extension of the author's 'thermokinetic principle' (1, 374; 3, 51, 52) to solutions. As a mathematician, the author is to be classed with Duhem rather than with Helmholtz or van 't Hoff. By this is meant that he is perfectly satisfied to indicate a result rather than to throw it into a form in which it is susceptible of quantitative experimental test. To give a concrete case, the author has deduced a pair of equations which apply to the evaporation of solutions. Now we know that the rate of evaporation of a solution is a function of the pressure difference, and we suspect that it is not a function of that alone. What the experimenter wants is an equation showing how the rate of vaporization should change with the surface-tension. In other words, given two aqueous solutions with non-volatile solutes, the solutions to have the same vapor-pressure but different surface-tensions, what will be the relative rates of vaporization in presence of the same sulfuric acid solution? The theory of this is hidden away in the author's equations, but it is pretty thoroughly hidden.

W. D. B.

On the atomic weight of the metal in radio-active barium chlorid. *S. Curie. Comptes rendus,* 129, *760* (*1899*). — The apparent atomic weights of barium in barium chlorid containing increasing amounts of radium were 140, 140.9, and 145.8, while experiments on inactive barium chlorid gave 138.1, 137.6, and 137.8.

W. D. B.

On a new radio-active substance. *A. Debierne. Comptes rendus,* 129, *593* (*1899*). — The author has succeeded in obtaining from pitch-blende a substance which shows one hundred thousand times the activity of uranium and which is entirely different in chemical properties from radium or polonium.

W. D. B.

On the mass of a cubic decimeter of water. *C. Fabry, J. Macé de Lépinay and A. Pérot. Comptes rendus,* 129, *709* (*1899*). — The mass of a cubic decimeter of water at 4° is now believed to be 999.9786 g with an error of only a few milligrams. This is nearly thirty milligrams higher than the earlier value (1, 246) which was then believed to be accurate to within six milligrams. *W. D. B.*

Reply to Professor Kahlbaum. *H. Debus. Zeit. phys. Chem.* 30, *556* (*1899*). — The author looks upon Kahlbaum's criticisms (4, 45) as unjust. *W. D. B.*

On some alkaloids of opium. *E. Leroy. Comptes rendus,* 129, *220* (*1899*). — Thermochemical data. *W. D. B.*

Investigations on the metallic derivatives of acetylene. *M. Berthelot and M. Delépine. Comptes rendus,* 129, *361* (*1899*). — Thermochemical data. *W. D. B.*

Studies on the isomerism of the sulfocyanates. *M. Berthelot. Comptes rendus,* 130, *441* (*1900*). — Thermochemical data. *W. D. B.*

Salicylic and para-oxybenzoic aldehydes, and salicylhydramid. *M. Delépine and P. Rivals. Comptes rendus,* 129, *520*; *Bull. Soc. Chim. Paris* (*3*) 21, *939* (*1899*). — Thermochemical data. *W. D. B.*

On the heat of oxidation of tungsten. *M. Delépine and L. A. Hallopeau. Comptes rendus,* 129, *600*; *Bull. Soc. Chim. Paris* (*3*) 21, *945* (*1899*). — Thermochemical data. *W. D. B.*

On the mercury alkyls. *M. Berthelot. Comptes rendus,* 129, *918* (*1899*). — Thermochemical data. *W. D. B.*

Lactic acid. *M. Berthelot and M. Delépine. Comptes rendus,* 129, *920* (*1899*). — Thermochemical data. *W. D. B.*

On the hydrate of sodium peroxid and the preparation of hydrogen peroxid. *de Forcrand. Comptes rendus,* 129, *1246* (*1899*). — Thermochemical data. *W. D. B.*

Investigations in the uric series. *M. Berthelot. Comptes rendus,* 130, *360* (*1900*). — Thermochemical data. *W. D. B.*

On a modification of the Sprengel pycnometer. *A. Minozzi. Rend. Accad. Lincei* (*5*) 8, *I*, *450*; *Gazz. chim. Ital.* 29, *I*, *406* (*1899*). — In the Ostwald-Sprengel pycnometer, liquid may flow out if the measurements are made at zero and the weighings at 20°. Instead of having the short arm run horizontally, the author extends it vertically, spreads it out, and puts in a stopper. In other words, it is a specific gravity bottle with a capillary constriction in the neck and a capillary arm starting from the bottom. *W. D. B.*

Comparison of different forms of heat insulation. *W. Hempel. Ber. chem. Ges. Berlin,* 31, *2994* (*1898*); *Wied. Ann.* 68, *137* (*1899*). — The author has determined the rate at which a mixture of solid carbonic acid and ether warms up when protected in different ways. The most effective protection is given by a first-class silvered vacuum tube; but ordinary vacuum tubes are less effective than a packing with eider-down, pure dry wool, silk, or cotton. Of these last, the eider-down and the wool are the most effective. *W. D. B.*

One-Component Systems

On the solidification of hydrogen. *J. Dewar. Comptes rendus,* 129, *451* (*1899*). — Solid hydrogen was obtained by placing a tube containing liquid hydrogen inside a second tube in which liquid hydrogen was distilling under diminished pressure. The temperature of the triple point is about −256°–257° and the pressure is 55 mm. On evaporating solid hydrogen under diminished pressure, a further drop of 2°–3° was obtained. *W. D. B.*

On the inversion temperature for the two forms of mercuric iodid. *D. Gernez. Comptes rendus,* 129, *1234* (*1898*). — The author finds the triple point for mercuric iodid at about 126°. He is evidently not familiar with the work of Schwartz. *W. D. B.*

Physical chemical studies on tin. *E. Cohen and C. van Eyk. Zeit. phys. Chem.* 30, *601* (*1899*). — Part of this paper has already been reviewed (4, 46) from a preliminary communication. This is the full paper. The most interesting of the new facts is that ordinary tin can be converted into gray tin by inoculating with the latter. When this happens accidentally in a storage warehouse, the spread of the infection is prevented by placing the blocks of tin in the direct sunlight until the gray form has disappeared. *W. D. B.*

On the limits of the solid state, III. *G. Tammann. Wied. Ann.* 68, *553, 629* (*1899*). — The author has made observations on naphthalene, water, carbon dioxid, ethylene dibromid, hydrocyanic acid, hydrated calcium chlorid, methyl mustard oil, *p*-xylene, diethylamin, dimethylethyl carbinol, trimethyl carbinol, acetic acid, sulfur, sodium, mercury, hexachlorethane, ammonium nitrate, silver iodid. As the manometer has been calibrated these results are the most accurate that the author has obtained. There is evidence of the existence of maximum melting-points in the case of naphthalene, carbonic acid, ethylene dibromid, hydrated calcium chlorid, hydrocyanic acid, acetic acid, and dimethylethyl carbinol. Triple points with two solid phases in equilibrium with a liquid were realized with carbon dioxid, acetic acid, trimethyl carbinol, and sulfur, the pressure in this last case being 1320 kg and the temperature 151°. Under a pressure of 930 kg and at a temperature of 64.2° three solid modifications of ammonium nitrate can coexist in stable equilibrium. *W. D. B.*

On the change of the heat of fusion along the cryobaric curve. *G. Tammann. Wied. Ann.* 67, *871* (*1899*). — Mathematical considerations with regard to the heat of fusion, intended to prove that there can be no critical point for solid and liquid. *W. D. B.*

Conversion of styrene into metastyrene under the influence of light. *G. Lemoine. Comptes rendus,* 129, *719* (*1899*). — The change of styrene into metastyrene (3, 115) takes place with a moderate rapidity in sunlight at ordinary temperatures and with phenomenal slowness in the dark. *W. D. B.*

On the pressure of saturated water-vapor at temperatures below 0°. *M. Thiesen. Wied. Ann.* 67, *690* (*1899*). — Since the vapor-pressure of water and ice are the same at the triple point and would be the same (both nothing) at the absolute zero, there must be an intermediate temperature for which the pressure difference is a maximum. From the author's calculations, this maximum should occur at $-11.7°$. *W. D. B.*

On the value of the internal pressure in the equations of van der Waals and of Clausius. *D. Berthelot. Comptes rendus*, 130, *69* (*1900*). — The author shows that the critical isotherm of van der Waals agrees with the experimental critical isotherm for carbon dioxid over half the curve, while the corresponding expression of Clausius represents the facts over the other half the curve. It is stated that a further complication gives a formula which describes the whole isotherm. The change consists in replacing the V^2 of the van der Waals formula by $V^2 + 2lVb + mb^2$. *W. D. B.*

On the critical condition. *C. Dieterici. Wied. Ann.* 69, *685* (*1899*). — From the observations of Ramsay and Young, the ratio of the ideal critical volume calculated by the gas law to the actually determined critical volume is obtained for a large number of substances. This ratio is found to vary considerably, but in the mean is equal to 3.75, which is considered by the author to be the correct value for all substances not undergoing a chemical change when in the critical state. From a consideration of van der Waals's equation of condition

$$(p + \pi)(v - b) = R\theta,$$

this ratio comes out 2.67, a value considerably lower than the observed value. In the light of the more recent modifications to the equation introduced by Lorenz, van der Waals, Jäger and Boltzmann, this ratio works out to be equal to 3. From a study of the behavior of water vapor between 0° and 200° C the author finds that the additional pressure necessary to conform to the ideal gas law may be expressed $\pi = \frac{a}{v^{\frac{5}{3}}}$. Substituting this for the term used in van der Waals's equation as the cohesion pressure and assuming the term b constant, the author finds the ratio equal to 3.75. Treating the condition equation in another way and taking

$$p = \frac{R\theta}{(v-b)} - \frac{a}{v^{\frac{5}{3}}},$$

and assuming b as the function of v, the author finds that it may be expressed

$$\frac{p_x v_x}{R\theta_x} = \frac{v_x}{v_0} = \left(\frac{v}{v-b}\right)_x \left\{ 1 - \tfrac{3}{5}(1 - b') \left(\frac{v}{v-b}\right)_x \right\},$$

where the suffix x refers to the critical condition. This gives, on the assumption of $b =$ a constant, the ratio

$$\frac{v_0}{v_x} = 3.75,$$

where v_0 is the ideal critical volume. Again treating the equation from the point of view of the kinetic gas theory he finds

$$\frac{v_0}{v_x} = \left(\frac{v-b}{v}\right)_x e^{\frac{v_x}{v_x - b_x}(1-b')},$$

from which the ratio comes 3.695. *H. T. B.*

On the co-volume in the equation characteristic of liquids. *D. Berthelot. Comples rendus*, 130, *115* (*1900*). — The author proposes to amend the van der Waals formula by considering b as a function of the temperature. If b_T is the co-volume at the temperature T, b_c the co-volume at the critical temperature T_c, the author writes

$$b_T = b_c\left[1 + 0.3\left(\frac{T}{T_c} - 1\right)\right].$$

W. D. B.

On association in liquids. *D. Berthelot. Comples rendus*, 130, *565* (*1900*). — Using the author's modifications of the van der Waals formula (preceding review), the author finds that carbon bisulfid and ethyl chlorid are not associated. There is ten to twenty-five percent association at the critical temperature with propyl, ethyl, and methyl alcohols. Since these substances follow the law of corresponding states, the conclusion would seem justified that the degree of association varies but slightly with the temperature. *W. D. B.*

On the dissociation of nitrogen peroxid. *A. Pochettino. Rend. Accad. Lincei.* (*5*) 8, *I*, *183* (*1899*). — The author has determined the ratio of the specific heats of nitrogen peroxid at different temperatures by the method of Kundt. The value increases with rising temperature, but so does the dissociation. Calculation showed that the observed values of the ratio k could be considered as the resultant of the values for NO_2 and N_2O_4. *W. D. B.*

Remarks on the kinetic theory of polyatomic gases and on the laws of Dulong and Petit. *F. Richarz. Wied. Ann.* 67, *702* (*1899*). — Priority reclamation against Staigmüller (3, 560). *W. D. B.*

Ratio of the specific heats of some saturated hydrocarbons. *A. Daniel and P. Pierron. Bull. Soc. Chim.* (*3*) 21, *801* (*1899*). — Using the method of Kundt, the authors find 1.225, 1.153, 1.108 for the ratio of the specific heats of ethane, propane, and isobutane respectively. *W. D. B.*

On the kinetic theory of liquids. *G. Jäger. Wied. Ann.* 67, *894* (*1899*). — Priority reclamation against Dieterici (3, 244) and reply to some comments by Voigt. *W. D. B.*

The kinetic theory of liquids. *W. Voigt. Wied. Ann.* 68, *139* (*1899*). — Reply to Jäger (preceding review). *W. D. B.*

On the kinetic theory of liquids. *G. Jäger. Wied. Ann.* 68, *615 1899*. — Rejoinder to Voigt (preceding review). *W. D. B.*

Rejoinder. *W. Voigt. Wied. Ann.* 69, *324* (*1899*). — Counter rejoinder to Jäger (preceding review). *W. D. B.*

On the absolute thermal expansion of liquids, and a method for increasing the effect. *G. Guglielmo. Rend. Accad. Lincei* (*5*) 8, *II*, *271*, *310* (*1899*). — Instead of the U-tube of Dulong and Petit, the author uses the spiral with rectangular sides, arranged vertically and horizontally. One-half of the spiral is heated to one temperature, the other half to another temperature, and the difference of levels in the two free ends noted. *W. D. B.*

On the temporary and residual changes in reversible nickel steels. *C. E.*

Guillaume. Comptes rendus, 129, *155* (*1899*).—Although a bar of nickel steel tends to assume a definite length for each temperature, this length is also a function of its previous history. Thus, a bar raised directly from 0° to 100° does not have the same length as the bar raised from 0° to 100° in twenty degree stages. The author finds that, with a well-seasoned bar, the changes on twenty degree rises can be expressed very accurately by an exponential formula.

W. D. B.

On the preparation and properties of the arsenids of strontium, barium, and lithium. *P. Lebeau. Comptes rendus*, 129, *47* (*1899*).—The arsenates were reduced by electrolytically heated carbon. *W. D. B.*

Two-Component Systems

On fixed inversion points. *H. Le Chatelier. Comptes rendus*, 129, *497* (*1899*).—The author calls attention to the fact that the phase rule applies only when we can neglect the surface-tension, when no one of the phases is infinitely small in amount, etc. It seems to him quite possible that a dissociating compound might break up in such a way as to form an infinite number of small particles, no one of which had the properties of matter in mass. Under these circumstances, the dissociation pressure need not have a unique value at any given temperature. The object of this hypothesis is to account for the behavior of iron and nickel in not losing their magnetic properties at a given temperature. This is very ingenious, but unfortunately the author cites in confirmation of his views the indefinite melting-point of vitreous substances, the variable melting-points of some compounds, and the varying vapor-pressure of the zeolites, all cases which are perfectly intelligible as they stand. Vitreous compounds are not solids and therefore have no melting-point. The variable melting-points of some compounds are due to dissociation, etc., and disappear if the system is allowed to reach equilibrium. The zeolites are solid solutions and there is no reason why the vapor-pressure should be constant at constant temperature.

W. D. B.

On the changes of state of iron and steel. *H. Le Chatelier. Comptes rendus*, 129, *279* (*1899*).—The phases at the point of recalescence of iron are said to be iron, the carbid Fe_3C, and a solid solution. When followed volumetrically, the change apparently consists in a contraction at about 775°, followed immediately by an expansion of such a nature that the curve from 860° upward is a prolongation of the curve up to 760°. As the author points out, this phenomenon has no known analogue. [The simplest explanation would be that a contraction takes place at the quadruple point and that the coefficient of expansion above this temperature is greater than below it. On this hypothesis, the coincidence of the two curves would be apparent and not real.]

The author was not able to observe any volumetric disturbances when iron loses its magnetism; with nickel, he believes that the magnetic properties are lost continuously between 350° and 380°. The upper temperature at which the change takes place with iron is subject to remarkable fluctuations even in the same sample of iron. The disturbing factors have not yet been recognized.

W. D. B.

On the expansion of iron and steel at high temperatures. *H. Le Chatelier. Comptes rendus*, 129, *331* (*1899*). — Below the transformation point, the coefficient of expansion of iron and steel is practically independent of the amount of carbon, but this ceases to be the case at higher temperatures; the coefficient increasing with increasing percentage of carbon. *W. D. B.*

Remarks on the use of cryohydrates. *A. Ponsot. Comptes rendus*, 129, *98* (*1899*). — The author records the fact that impure salts do not give the same cryohydric temperatures and concentrations as pure salts, that he has used twenty-six different salts in making cryohydric baths, and that it is possible to produce fluctuations in the temperature of a cryohydric mixture if it be heated or cooled too rapidly. *W. D. B.*

On the dissociation of ammoniacal mercuric iodid. *M. François. Comptes rendus*, 129, *296* (*1899*). — The compound $HgI_2 2NH_3$ loses ammonia, forming $3HgI_2 4NH_3$, and this latter compound then passes into HgI_2. The author has determined the dissociation pressure for the two univariant systems between 15° and 80°. *W. D. B.*

Compounds of lithium chlorid with ethylamin. *H. Bonnefoi. Comptes rendus*, 129, *1257* (*1899*). — Lithium chlorid crystallizes with one, two, and three of ethylamin. The author has determined some dissociation pressures. *W. D. B.*

On the true and apparent freezing-point and on cryoscopic methods. *M. Wildermann. Zeit. phys. Chem.* 30, *577* (*1899*). — The most interesting, though perhaps not the most instructive, feature of the paper is that the author's method cannot possibly give errors exceeding a ten-thousandth of a degree. *W. D. B.*

Antimony trichlorid as a cryoscopic solvent. *S. Tolloczko. Zeit. phys. Chem.* 30, *681* (*1899*). — A number of organic substances are soluble in antimony trichlorid and give normal depressions of the freezing-point. Many inorganic salts are insoluble; but not potassium chlorid and potassium bromid. Both of these give results pointing to dissociation, the apparent dissociation being more than double with potassium bromid what it is with potassium chlorid [formation of $SbBr_3$?]. The author recommends antimony trichlorid as a cryoscopic solvent for organic substances owing to the high value, 184, of the constant. *W. D. B.*

On the molecular weight of some elements and some of their derivatives. *G. Oddo and G. Serro. Rend. Accad. Lincei*, (*5*) 8, *II*, *281*; *Gazz. chim. Ital.* 29, *II*, *343* (*1899*). — In carbon bisulfid, benzene, and ethyl alcohol, iodin gives values corresponding to the formula I_2; in carbon tetrachlorid, the apparent formula is I_3. Sulfur behaves like S_8 in boiling carbon tetrachlorid, phosphorus pentachlorid behaves like PCl_3 in the same solvent, while iodin monochlorid and iodin trichlorid lower the boiling-point. *W. D. B.*

Polymerization of some inorganic oxychlorids. *G. Oddo and E. Serra. Rend. Accad. Lincei*, (*5*) 8, *II*, *244*; *Gazz. chim. Ital.* 29, *II*, *318* (*1899*). — $POCl_3$, $SOCl_2$, $POBr_3$, $PSCl_3$, and CrO_2Cl_2 give molecular weights corresponding to the formula weights when determined in freezing benzene and values approximately double the formula weights when determined in boiling benzene. This would appear to point to a polymerization with rising temperatures.

W. D. B.

On physical equilibrium in mixtures of isomorphous substances. *G. Bruni and F. Gorni. Rend. Accad. Lincei,* (*5*) 8, *II, 181* (*1899*). —Continuous freezing-point curves passing through minimum temperatures were obtained with *p*-dichlorbenzene and *p*-chlorbrombenzene. with *p*-dichlorbenzene and *p*-dibrombenzene, and with azobenzene and dibenzil.

The author discusses again the theoretical impossibility of Küster's hypothesis that isomorphous mixtures may have constant freezing-points. Since the author's proof has been accepted by Duhem, it may be well to consider what can actually be proved, more especially since the objections of the reviewer (3, 245) were not properly formulated. Gibbs proved that, at constant pressure, the two phases of a two-component system can have the same composition only when the temperature is a maximum or a minimum (or both?). Küster's hypothesis cannot therefore be true for a two-phase system under constant pressure. The difference in the composition of the coexisting phases may, however, be infinitely small along the whole curve, and this difference might conceivably, though not probably, disappear for the system, solid, liquid, and vapor, where the pressure is not constant. Bruni is undoubtedly right experimentally, but his thermodynamic proof does not apply theoretically to the experiments of Küster. *W. D. B.*

Solid solutions and isomorphous mixtures in saturated and unsaturated compounds with open chains. *G. Bruni and F. Gorni. Rend. Accad. Lincei,* (*5*) 8, *I, 454, 570* (*1899*); *Gazz. chim. Ital.* 30, *I, 55* (*1900*). — It is postulated that substances of analogous composition have a tendency to form solid solutions. It is then shown that chlorbromethane gives anomalous results with dibromethane. Dimethyl fumarate gives abnormal values in dimethyl succinate, while the dimethyl ester of maleic acid does not. Similarly, crotonic acid is abnormal in butyric acid and isocrotonic acid normal. Cinnamic acid raises the freezing-point of phenyl propionic acid, while allocinnamic acid gives normal lowerings. In azobenzene, benzilidene aniline is very abnormal, while stilbene raises the freezing-point. It is clear that the authors are working along a very promising line. *W. D. B.*

Solid solutions and isomorphous mixtures. *G. Bruni. Rend. Accad. Lincei,* (*5*) 8, *II, 212*; *Gazz. chim. Ital.* 29, *I, 149* (*1899*). —The author discusses at length Küster's hypothesis that isomorphous mixtures are not solid solutions and reaches the only possible, rational conclusion that this distinction is not sound. *W. D. B.*

On the cryoscopic behavior of substances having a constitution like that of the solvent. *F. Garelli and F. Calzoari. Rend. Accad. Lincei,* (*5*) 8, *I, 579; II, 58*; *Gazz. chim. Ital.* 29, *II, 258, 357* (*1899*). —Menthol is slightly abnormal in thymol. Stilbene and dibenzil give a single freezing-point curve, which is not a straight line. Azobenzene, benzilanilin, and benzilidene anilin are abnormal in dibenzil; but the slight variation in the case of the benzilanilin is perhaps due to the NH group. Dibenzil, stilbene, azobenzene, and benzilidene anilin are practically normal in benzilanilin. Triphenylamin is slightly but distinctly abnormal in triphenyl methane.

In the second paper are some fifteen experiments, undertaken to test the general rules previously laid down by Garelli, [Zeit. phys. Chem. 3, 4 (1894); 18, 59 (1895); 21, 113 (1896)]. Three exceptions were found. Orthonitrophenol is normal in nitrobenzene; the 2-4-dinitrophenol in metadinitrobenzene; and *p*-amido-acetophenol in acetophenol. *W. D. B.*

On the mutual solubility of liquids. *G. Bruni. Rend. Accad. Lincei*, (*5*) 8, *II, 141* (*1899*); *Gazz. chim. Ital.* 30, *I, 25* (*1900*). — As yet no case has been found experimentally of a binary system in which the concentration-temperature curve for two liquid phases in equilibrium with vapor is entirely closed. A closed curve has been realized by the author with a system containing 1.5 percent of ethyl alcohol and varying relative quantities of methyl ethyl ketone and water. The theorem of the rectilinear diameter applies with a considerable degree of accuracy. *W. D. B.*

On the vapor-pressure of coexistent phases. *M. Cantor. Wied. Ann.* 67, *683* (*1899*). — The author points out the fallacy in the assumption that two liquid phases in equilibrium give off the same vapor. The line of argument is that previously adopted by the reviewer. The author then discusses the condition under which the two phases would give off the same vapor and reaches the conclusion that this will be true only when the two liquid phases have the same surface-tension. *W. D. B.*

On the vapor-pressures of dilute aqueous solutions. *C. Dieterici. Wied. Ann.* 67, *859* (*1899*). — The author has repeated some of his earlier measurements. His results are now said to be accurate to ±0.001 mm Hg. Since this corresponds to about a ten percent error in the molecular depression of dilute solutions, no conclusions are binding. *W. D. B.*

On some properties of dioxyacetone in relation to its degree of association. *G. Bertrand. Comples rendus*, 129, *341* (*1899*). — Dioxyacetone $CH_2OH.CO.CH_2OH$ is a solid obtained by oxidizing glycerol. It melts at 70° and is prone to surfusion. The supercooled melt is readily soluble in cold absolute alcohol, ether or acetone, while the crystals are not. When first dissolved in water, the crystals lower the freeeing-point by an amount corresponding to the molecular weight 180 instead of 90. If the solution be allowed to stand at about 15°, the limiting apparent molecular weight is 91–93; at 0° equilibrium is reached when the apparent molecular weight is 96–97. *W. D. B.*

Absorption, III. *J. M. van Bemmelen. Zeit. anorg. Chem.* 18, *98* (*1898*). — This paper deals with the air-spaces that form when the silicic acid gel loses water, with the loss of absorption power in colloids, and with the change of crystalline hydrates into amorphous substances. The silicic acid gel loses water under continuously diminishing pressure with no formation of air-spaces when no second colloid modification is formed. The air-spaces appear when the change to the second colloid modification takes place. As the vapor-pressure curves for the two modifications are not the same, dehydration and taking up water occur at different pressures along a portion of the isotherm. The effect of time during the dehydration is to cause a change into the second colloid modification before the dehydration has proceeded quite so far. Heating to a high temperature causes a loss of absorbing power in most cases. If crystallized beryllium or aluminium hydroxid be heated to about 200°, they change into amorphous colloids. The general theory of these phenomena has recently been discussed by Duhem (4, 65). *W. D. B.*

Absorption. IV. *J. M. van Bemmelen. Zeit. anorg. Chem.* 20, *185* (*1899*). — The ferric oxid gel loses water under a continuously changing pressure, and the assumption of a tetrahydrate is based on an analysis under fortuitous hygroscopic conditions. The peculiar hysteresis phenomena observed with the silicic acid and copper oxid gels are to be found in this case also. *W. D. B.*

On the determination of the coefficient of solubility of liquids. *A. Aignan and E. Dugas. Comptes rendus*, 129, *643* (*1899*). — Because amyl alcohol dissolves in water with contraction, the authors consider that a hydrate is formed and they look upon this hypothesis as proved because the solubility of amyl alcohol in water decreases with rising temperature. *W. D. B.*

On the liquefaction of gaseous mixtures. *F. Caubet. Comptes rendus*, 130, *167* (*1900*). — The author has determined and shown in a cut the dew-lines and boiling curves for ten mixtures of methyl chlorid and carbon dioxid. In all cases there is retrograde condensation. *W. D. B.*

Numerical laws of chemical equilibrium. *O. Boudouard. Comptes rendus*, 130, *132* (*1900*). — It is shown that the displacement with the temperature of the equilibrium between carbon monoxid and carbon dioxid in presence of carbon can be represented by the van 't Hoff formula, assuming a constant heat of reaction. *W. D. B.*

On the molecular volumes of some derivatives of camphor. *A. Haller and P. T. Müller. Comptes rendus*, 130, *221* (*1900*). — The differences between the molecular volumes obtained from quarter-normal toluene solutions and those calculated by Traube's formula are eliminated if we allow a decrement of 23 cc for each benzene ring. *W. D. B.*

On the composition by volume of hydrofluoric acid. *H. Moissan. Comptes rendus*, 130, *544* (*1900*). — Hydrofluoric acid was electrolyzed, the fluorin led into water and the amount of oxygen evolved was compressed with the amount of hydrogen given off at the cathode. The volume of the hydrogen was twice the volume of the oxygen within the limits of error, as of course it must be. In some unexplained way, the author takes this to be a proof that gaseous fluorin has the formula F_2. In the second experiment a known volume of dry fluorin in a glass vessel was brought in contact with water and the resulting oxygen measured. This was very nearly half the volume of the fluorin. Since Thorpe and Hambly found a vapor density for hydrofluoric acid above 88° corresponding to the formula HF, we are justified in concluding that above 88° one volume of hydrogen unites with one volume of fluorin to form two volumes of hydrofluoric acid. *W. D. B.*

Contributions to our knowledge of platinum tetrachlorid. *A. Miolati. Zeit. anorg. Chem.* 22, *445* (*1899*). — The author has studied the solution of platinum tetrachlorid in water from several points of view, and shows that a dibasic acid is formed which probably has the formula $H_2PtCl_4(OH)_2$, though the formula H_2PtCl_4O is not absolutely excluded. *W. D. B.*

Poly-Component Systems

Application of the phase rule to alloys and rocks. *H. Le Chatelier. Comptes rendus,* 130, *85* (*1900*). — It is pointed out that if we find a number of phases equal to or greater than $n + 2$, the system is not in equilibrium and must have been formed rapidly. Illustrations are cited from alloys and rocks. *W. D. B.*

On cryohydric phenomena in solutions of enantiomorphous isomers. *G. Bruni. Rend. Accad. Lincei.* (*5*) 8, *I, 332* (*1899*); *Gazz. chim. Ital.* 30, *I, 35* (*1900*). — The author points out that from the form of the cryohydric curves in ternary systems one can tell whether two of the components form a conglomerate, a racemic compound, or a continuous series of mix-crystals. *W. D. B.*

On the allotropy of benzophenone. *Oechsner de Coninck. Comptes rendus,* 130, *40* (*1900*). — The author dissolved benzophenone in aqueous alcohol and passed 1400 liters of air through the solution for six weeks. At the end of three weeks, the benzophenone obtained by evaporation of the solution to dryness showed the original melting-point. Later portions showed a change and at last the instable form was obtained pure. The benzophenone was not oxidized by the air current. *W. D. B.*

Volumetric analysis of hydrogen, and chemical tensions. *A. Colson. Comptes rendus,* 130, *330* (*1900*). — Hydrogen is absorbed practically quantitatively at 0° by silver hydroxid. At constant pressure the rate of absorption is approximately constant. *W. D. B.*

Reciprocal displacement of metals. *A. Colson. Comptes rendus,* 129, *825* (*1899*). — Between 150° and 350° in the vacuum of a Crookes tube, the reaction $HgS + 2Ag = Hg + Ag_2S$ is reversible. In the discussion the author overlooks the fact that silver is soluble in mercury. At 350° the reaction $Cd + CuS \rightleftarrows Cu + CdS$ is also reversible. *W. D. B.*

On chemical equilibrium in a system containing four gaseous components. *H. Pélabon. Comptes rendus,* 130, *576* (*1900*). — A preliminary note to the effect that the mass law relations apply in the case of the reaction.

$$HgSe + H_2 \rightleftarrows H_2Se + Hg.$$

W. D. B.

On the action of dry hydrochloric acid on silver and the reverse reaction. *Jouniaux. Comptes rendus,* 129, *833* (*1899*). — Hydrogen acts on silver chlorid at temperatures above 200°, but the reaction does not run to an end. Hydrochloric acid attacks silver above 400° but the reaction does not run to an end. Above 600° the same equilibrium is reached whether starting with one system or the other. Below 600° this is not the case and we therefore get the two curves characteristic of false equilibrium. *W. D. B.*

Dissociation of ammonium and potassium mercuric iodids by water. *M. François. Comptes rendus*, 129, *959* (*1899*). — The double iodids of mercury and ammonium and of mercury and potassium are decomposed by water with precipitation of mercuric iodid. *W. D. B.*

Action of concentrated ammonia on ammoniacal mercuric iodid. *M. François. Comptes rendus*, 130, *332* (*1900*). — The author has determined the part of the 20° isotherm along which $HgI_2 2NH_3$ is solid phase. *W. D. B.*

On the reducibility of metallic oxids. *H. Hélier. Bull. Soc. Chim. Paris*, (*3*) 21, *43* (*1899*). — Because litharge loses its oxygen continuously when heated higher and higher in a current of hydrogen, the author concludes that litharge is a polymer, having the formula $(PbO)_n$ and that it depolymerizes in many stages. [It is more probably a case of solid solution.] *W. D. B.*

On chromic acetate. *A. Recoura. Comptes rendus*, 129, *158*, *288* (*1899*). — The author shows the existence of four chromic acetates: the triacetate, green in solution; the diacetate plus one of acetic acid, violet in solution; the monoacetate plus two of acetic acid, violet in solution; the monoacetate plus two of acetic acid, green in solution. The existence of these four forms was shown by titration and by cryoscopic determinations. The first is quite instable and changes rapidly into the second, which latter changes slowly into the third. The change of the third form into the fourth takes about a year at ordinary temperatures; but is very rapid when the solution is boiled.

W. D. B.

On the reversible liquefaction of albuminoids. *Tsvett. Comptes rendus*, 129, *551* (*1899*). — Gelatine will dissolve readily in a concentrated aqueous solution of resorcin and will precipitate from the solution. Pyrocatechuic acid, phenol, chloral hydrate, etc. may be substituted for the resorcin, and many other albuminoids, though not all, for the gelatine. *W. D. B.*

On the determination of sulfuric acid in the presence of iron. *F. W. Küster and A. Thiel. Zeit. anorg. Chem.* 22, *424* (*1899*). — It is shown that the iron in the barium sulfate precipitate is present in the form of $Ba[Fe(SO_4)_2]_2$, a complex salt which is formed with a relatively low velocity and which is more stable in hot solutions than in cold. The authors show further that this hypothesis enables them to account for all the discrepancies due to slight differences in manipulation. The formation of the complex salt and the resulting error in analysis can be avoided by precipitating in the cold; by precipitating hot, in case the sulfate solution is added to the barium chlorid solution instead of the other way round; by removing the ferric ions before precipitating. This last can be done in two ways, by precipitating the iron with ammonia or by forming complex ions through addition of ammonium oxalate or other salts.

This is a very creditable piece of work and may well be taken as typical of the way in which analytical reactions should be studied. *W. D. B.*

Preparation of ozone by the action of fluorin on water. *H. Moissan. Comptes rendus*, 129, *570* (*1899*). — When fluorin acts on water at 0° there is formed hydrofluoric acid and ozone. In this way a gas can be obtained showing a high percentage of ozone. It did not occur to the author to determine whether there was any quantitative relation between the amount of hydrofluoric acid and the amount of ozone. *W. D. B.*

Action of hydrofluoric acid and of fluorin on glass. *H. Moissan. Comptes rendus,* 129, *799* (*1899*). — Anhydrous hydrofluoric acid does attack glass, the experiments of Louyet to the contrary notwithstanding. On the other hand, clean dry glass is not attacked by pure fluorin. Traces of hydrofluoric acid bring about an action. *W. D. B.*

On the position of the magnetic inversion points in nickel steels. *L. Dumas. Comptes rendus,* 129, *42* (*1899*). — The authors have studied and tabulated the magnetic behavior at +15°, —78° and —188°, of steels containing varying amounts of carbon, silicon, manganese, nickel, and chromium. *W. D. B.*

On the simultaneous phenomena of oxidation and hydration in organic compounds under the influence of oxygen and light. *M. Berthelot. Comptes rendus,* 129, *627* (*1899*). — When ether, water, and air are exposed to sunlight, some acetic acid is formed, but the bulk of the reaction consists in the formation of ethyl alcohol. The same reactions take place in the dark, though less rapidly. *W. D. B.*

Action of magnesium on solutions of its salts. *G. Lamoine. Comptes rendus,* 129, *291*; *Bull. Soc. Chim. Paris,* (*3*) 21, *802* (*1899*).— Although magnesium decomposes water slowly, the decomposition becomes rapid in case a salt of magnesium be added. *W. D. B.*

The action of magnesium on salt solutions. *H. Mouraour. Comptes rendus,* 130, *140* (*1900*). — The author points out that other salts besides those of magnesium have the power of making magnesium react with water. *W. D. B.*

Osmotic Pressure and Diffusion

Relations between the diuretic actions and osmotic properties of sugars. *E. Hédon and J. Arrons. Comptes rendus,* 129, *778* (*1899*). — It was found that the solutions of different sugars, which have the same diuretic effect, are isotonic. *W. D. B.*

On the theory of diffusion. *O. Wiedeburg. Zeit. phys. Chem.* 30, *586* (*1899*). — Bose's calculations (4, 326) were made on the assumption of diffusion between two constant concentrations. This being difficult to realize experimentally, the author points out how an approximate calculation can be made for varying concentrations. *W. D. B.*

Velocities

On the kinetics of simultaneous reactions. *R. Wegscheider. Zeit. phys. Chem.* 30, *593* (*1899*). — The author discusses the general form of the differential equations representing the reaction velocity in systems where two or more reactions can take place simultaneously. Only in special cases is it possible to express the results by means of a single differential equation containing but one variable besides the time. *W. D. B.*

Rate and limit of esterification of phosphoric acid by methyl alcohol. *G. Belugou. Bull. Soc. Chim. Paris,* (*3*) **21**, *166* (*1899*). —Phosphoric acid and methyl alcohol react almost instantaneously. On standing or on heating, the amount of ester formed apparently decreases. *W. D. B.*

Rate and limit of esterification of phosphoric acid by glycerol. *H. Imbert and G. Belugou. Bull. Soc. Chim. Paris,* (*3*), **21**, *935* (*1899*). — When phosphoric acid and anhydrous glycerol are mixed at different temperatures, the amount of ester formed fluctuates in an extraordinary manner with the time. The presumption is that there are at least two reactions taking place, the formation of ester and the dehydration of the phosphoric acid, but the author does not prove this except in so far as he shows that abnormal results disappear when water is added. *W. D. B.*

On the velocity of the explosion wave in acetylene. *M. Berthelot and H. Le Chatelier. Comptes rendus,* **129**, *427* (*1899*). — The rate of propagation of the explosion wave in acetylene varied in these experiments from 1000 to 1600 m/sec increasing with the pressure. A constant rate was not obtained. This may have been because the tubes were too short; but the authors incline to the view that acetylene differs radically from the other explosive mixtures already studied in that carbon is precipitated. The intense shattering effect of the acetylene explosion is attributed to the fact that the reaction runs to an end right from the start. *W. D. B.*

On the explosion of potassium chlorate. *M. Berthelot Comptes rendus,* **129**, *926* (*1899*). — An explosive reaction can be made to go slowly by keeping the temperature down, and a reaction which is ordinarily not explosive can therefore be made to go explosively by raising the temperature. This can be realized by dropping potassium chlorate into a test-tube heated to redness. It was realized experimentally on a large scale in England last year when a potassium chlorate factory was burned. *W. D. B.*

Electromotive Forces

A new (sixth) form of inversion cell. *E. Cohen. Zeit. phys. Chem.* **30**, *623* (*1899*). — Under this head comes a cell in which a stable and an instable modification of a metal form the electrodes while the electrolyte is a salt of the same metal. Tin is the only metal known as yet which is suitable for such a cell. The author deduces a relation between the electromotive force and the change of the inversion temperature with the pressure, which relation he proposes to test experimentally. *W. D. B.*

On the electromotive force of some concentration cells and of cells with zinc and copper electrodes in organic solvents. *R. Salvadori. Rend. Accad. Lincei,* (*5*), **8**, *I*, *452*; *Gazz. chim. Ital.* **29**, *I*, *498* (*1899*). — Merely some preliminary measurements for which no accuracy is claimed. *W. D. B.*

On the contact theory. *Q. Majorana. Rend. Accad. Lincei.* (*5*) **8**, *I*, *188*, *255*, *302*; *Nuovo Cimento,* (*4*) **9**, *335* (*1899*). — The author rotates strips of zinc and copper on an isolated disk inside a shell of zinc and copper. A commutator keeps the direction of the current constant and the author actually gets a continuous current passing through his galvanometer, the strength of the current varying with the velocity of rotation.

In another experiment the author silvered a quartz thread. On bringing a plate of silver near the thread there was no deflection. On bringing up a plate of zinc, aluminum or copper, the thread was attracted. *W. D. B.*

Experimental investigation into the cause of contact electricity. *C. Christiansen. Wied. Ann.* 69, *661* (*1899*). — This is the fourth communication of a series on contact electricity. In the present paper the effect of moisture on the potential difference between an amalgam and mercury in oxygen gas is dealt with. It is found that dry gas gives a much smaller and even negative potential compared to the value in moist gas. In dry air an oxide is formed on the surface of the amalgam, whilst in moist air a hydrate is formed. Part of the paper is devoted to the theory of the drop electrode, and the greater part to a description of the apparatus used in the present work. *H. T. B.*

On Liebenow's thermodynamic theory of theomoelectricity. *W. Voigt. Wied. Ann.* 69, *706* (*1899*). — The author gives a somewhat lengthy criticism of the theory proposed by Liebenow (4, 58), and points out that the ideas in the paper are not altogether clear, and that considerable guess work has to be used to arrive at the author's meaning. Nothing new is considered to have been advanced in Liebenow's paper, but that he has simply ratified old results in the old way. *H. T. B.*

On the variation of the Peltier effect in a magnetic field. *A. Pochettino. Rend. Accad. Lincei*, (*5*) 8, *II*, *50* (*1899*). — The author has studied the Peltier effect between copper and iron in a magnetic field of uniform but variable intensity. The coefficient increases from 0.008824 in a field of zero intensity to 0.008968 in a field of 98 units, and then decreases, reaching the normal value again in a field of about 345 units, and a value of 0.007304 in a field of 2000 units. The measurements were made at a temperature of 11°–14°. The coefficient is independent of the direction of magnetization. The Thomson-Houllevigue formula represents the facts up to a field of 700 units. *W. D. B.*

On the measurement of the electrical constants with periodically changing currents. *C. Heinke. Wied. Ann.* 69, *612* (*1899*). — This paper is of technical interest only. *H. T. B.*

On the degree of magnetization of water. *G. Jäger and S. Meyer. Wied. Ann.* 67, *707* (*1899*). — Further experiments have strengthened the belief of the authors in the accuracy of their previous conclusions (3, 428). *W. D. B.*

Electrolysis and Electrolytic Dissociation

On the behavior of an iron anode in a solution of sodium acetate and acetic acid. *G. Arth. Bull. Soc. Chim. Paris*, (*3*) 21, *766* (*1899*). — When a plate of very pure iron is made anode in a solution containing 50 g sodium acetate and 50 g acetic acid in a liter of water, the iron dissolves, forming ferrous acetate, provided the current density be low. If the current density is increased, the iron becomes passive and does not dissolve at all. Under certain other conditions not yet clearly defined, the iron dissolves forming ferric acetate. This would seem to be analogous to the behavior of chromium. *W. D. B.*

Electrolytic reduction of aliphatic nitro compounds. *P. Pierron. Bull. Soc. Chim. Paris,* (*3*) 21, *780* (*1899*). — The nitro compound is dissolved in sulfuric acid and alcohol, and electrolyzed with a cathode density 0.004-0.0075 amp/cm^2, using a nickel cathode. At 15°-20° hydroxylamin compounds are obtained, at 70° amin compounds. Experiments were made with nitromethane, nitroethane, and nitropropane. *W. D. B.*

On the electrolysis of potassium chlorid. *A. Brochet. Comptes rendus,* 130, *134* (*1900*). — The author has electrolyzed a potassium chlorid solution containing traces of potassium chromate and of caustic alkali. He gets an excellent efficiency at the anode; but he worked at 16°-20°, so that it is probable that his solution contained perchlorate as well as chlorate. *W. D. B.*

On crystallization of metals by electric transference in distilled water. *T. Tommasina. Comptes rendus,* 130, *325* (*1900*). — When a current of less than one milliampere is passed between two metallic electrodes standing in distilled water, arborescent crystals are obtained. *W. D. B.*

On apparatus for electrolysis. *J. Riban. Bull. Soc. Chim. Paris,* (*3*) 21, *81* (*1899*). — In order that the actual current density may be the same as the apparent current density the author recommends the use of concentric electrodes. *W. D. B.*

On the Wehnelt interrupter. *E. Rothé. Comptes rendus,* 129, *675* (*1899*). — If the current contain a sufficiently high resistance, the Wehnelt interrupter will not work. If the resistance be decreased gradually, there will suddenly come a point, 11.5 amp for the author's instrument, at which the interrupter begins to act, the current dropping to 2.5 amp. The resistance can then be increased without checking the action. A different result is thus obtained, depending on whether one starts with a small resistance and increases it, or starts at once with a high resistance. *W. D. B.*

On the Wehnelt interrupter. *R. Federico and P. Baccei. Rend. Accad. Lincei,* (*5*) 8, *347* (*1899*). — The interruptions do not occur at equal intervals and the time for which the current is really zero, is only about one-sixth of the interruption period. The number of interruptions varies with the electrolytes. Potassium bichromate and sulfuric acid are said to work much better than sulfuric acid alone. *W. D. B.*

Remarks to the paper by Simon "On a new fluid interrupter." *W. Ziegler. Wied. Ann.* 69, *718* (*1899*). — Fault is found with Simon for not having given sufficient credit in his paper (4, 158) to the author in his work with Richarz for certain ideas developed in regard to the local current heating in the Wehnelt interrupter. *H. T. B.*

Effect of dissociation on the toxicity of metallic salts. *L. Maillard. Bull. Soc. Chim. Paris,* (*3*) 21, *26* (*1899*). — Adding ammonium sulfate to a solution of copper sulfate forces back the dissociation of the latter salt and decreases its toxic action on *Penicillium glaucum.* *W. D. B.*

Investigations on the diamins. *M. Berthelot. Comptes rendus,* 129, *687, 694, 743* (*1899*). — In the second of these three notes, the author shows that diethylene diamin behaves like a bivalent base with methyl orange and like a univalent base with phenolphthalein. This is interesting as showing the change in the apparent sensitiveness in the case of the two indicators, since phosphoric acid acts like a monobasic acid in presence of methyl orange and like a dibasic acid in presence of phenolphthalein. The author, of course, suggests that the explanation is to be found in thermochemical data. The first and third notes deal with thermochemical data relative to diethylene diamin.

W. D. B.

Titration of amins. *A. Astruc. Comptes rendus*, 129, *1021* (*1899*). — The aliphatic amins act like univalent bases, both with methyl orange and with phenolphthalein. The aromatic amins, pyridin, quinolin, phenylhydrazin, and hydroxylamin are neutral with phenolphthalein but univalent bases with methyl orange.

W. D. B.

Acidimetry. *H. Imbert and A. Astruc. Comptes rendus*, 130, *35* (*1900*). —Phosphoric acid is monobasic with methyl orange, dibasic with phenolphthalein, and tribasic with Poirrier blue. The authors have tested these three indicators with other acids. The results are quite intelligible in the light of the dissociation theory, and it is interesting to note that *p*-oxybenzoic acid is dibasic with Poirrier blue.

W. D. B.

Heat of neutralization of hydrocarbonyl ferrocyanic acid compared with that of hydroferrocyanic acid. *J. A. Miller. Comples rendus*, 129, *962* (*1899*). — In dilute solutions, there is an evolution of about 14 Cal for each of the four hydrogens neutralizad in hydroferrocyanic acid and the same phenomenon is observed with each of the three hydrogens in $H_3FeCO(CN)_5$.

W. D. B.

Heat of neutralization and acidimetry of cacodylic acid. *H. Imbert. Comples rendus*, 129, *1244* (*1899*). — Cacodylic acid is neutral with methyl orange, monobasic with phenolphthalein; its heat of neutralization is 14.1 Cal.

W. D. B.

The effect of temperature on the electrical conductivity of dilute amalgams and on the solubility of metals in mercury. *Q. Larson. Drude's Ann.* 1, *123* (*1900*). — The author has determined the conductivities at different temperatures of varying solutions of lead, zinc, cadmium, tin, and bismuth in mercury. The conductivity for a given concentration increases very nearly proportionally to the temperature, and the proportionality factor increases with increasing concentration.

W. D. B.

On the relation between the fluidity and electrolytic conductivity of salt solutions; also on the conductivity of oleic acid and its alkali salts in water and alcohols at different temperatures. *R. Dennhardt. Wied. Ann.* 67, *325* (*1899*). — The objects of this paper are stated at length in the title. The results of the paper as summarized by the author are:

In concentrated solutions, there is no direct relation between fluidity and conductivity.

The maxima of molecular conductivity in the solutions of oleic acid in methyl and ethyl alcohol correspond to minima in the temperature coefficients and vice-versa. The molecular conductivities of oleates show minima in aqueous solutions, but not in pure alcoholic solutions.

The abnormal results of the oleates are due to hydrolysis.

In aqueous solutions, hydrolysis produces first the formation of colloidal acid oleate and then the free oleic acid.

No evidence could be found for the existence of basic oleates.

W. D. B.

Effect of X-rays on the electrical resistance of selenium. *Perreau. Comptes rendus*, 129, *956* (*1899*). — The electrical resistance of selenium spread on brass electrodes decreases when the selenium is exposed to X-rays. The change is reversible. *W. D. B.*

Dielectricity and Optics

On the dissipation of electrostatic charges by illumination. *O. Knoblauch. Zeit. Elektrochemie*, 6, 99; *Zeit. phys. Chem.* 29, *527* (*1899*). — A great many substances have been investigated with reference to their power to dissipate electrostatic charges under the influence of light. Attention is called to the fact that, in spite of the varied chemical nature of the substances, it is always a negative and never a positive charge which is destroyed. This suggests a common cause and the author finds this in the action on the substances of the oxygen in the air. The author's view is that the oxidation is preceded by a formation of negatively charged oxygen ions, and only negative electricity can be dissipated because the oxygen can only take up a negative charge. [In view of van 't Hoff's work on phosphorus, it would seem quite as reasonable to suppose that the negatively charged oxygen did the oxidizing and the positively charged oxygen was neutralized by the negative electrostatic charge.]

The experiments show that there is a relation, though not an absolute one, between sensitiveness to light and power to dissipate electrical charges. In many cases, it can be shown that the photoelectric dissipation is due to the oxidation of the illuminated substance. *W. D. B.*

On the dielectric cohesion of rarefied gases. *E. Bouty. Comptes rendus*, 129, *204* (*1899*). — It has been found (preceding review) that when a tube containing a rarefied gas is placed in a uniform electrostatic field, the gas behaves like a perfect dielectric until a critical intensity f is reached. The author finds that f can be stated as the following function of the pressure p of gas:

$$f = \mathrm{A}\left(1 + \mathrm{B}p + \frac{\mathrm{C}}{p}\right).$$

In this equation A increases with increasing molecular weight, while B and C appear to be independent of the nature of the gas. When p is expressed in millimeters of mercury we have approximately, $\mathrm{B}/\mathrm{C} = 4.4$. *W. D. B.*

On the formulas of Mossotti-Clausius and of Betti relative to the polarization of dielectrics. *F. Beaulard. Comptes rendus*, 129, *149* (*1899*). — In one particular experimental case it was found that the formulas of Mossotti-Clausius and of Betti both describe the facts satisfactorily. *W. D. B.*

On moving bodies in an electric field, and on the electric conductivity of atmospheric air. *A. Heydweiller. Wied. Ann.* 69, *531* (*1899*). — The author investigates the ponderomotive force in a rotating electric field of bodies suspended in a glass enclosure in air of different pressures from the point of view of the theoretical and experimental work of Hertz. Two forces are recognized in a rotating field, one depending on the conductivity, and the other on the dielectric properties of the suspended body. Whereas the former may produce either a retarding or an accelerating motion, the latter produces only a retardation. From theoretical considerations of experiments made on disks of copper, ebonite, paraffin and mica suspended in a glass cylinder, the conducting power of glass is given as 2×10^{-4} electrostatic units. The conducting power of air is found to depend very greatly on the field strength and on the density. It increases with increasing field and decreasing density. In the latter case it increases, passes through a maximum and decreases again. This maximum in the author's experiments appears at a pressure of 0.005 mm of mercury. A determination of the conductivity of air with a field of about 5 C. G. S. units was of the order of 10^{-1} electrostatic units. The author concludes the paper by considering the movements of the heavenly bodies as likely to be influenced by the forces under discussion. *H. T. B.*

Variation in the dielectric constant of glass under stress. *O. M. Corbino. Rend. Accad. Lincei*, (5) 8, *II*, *238* (*1899*). — The author defends his methods of measurement (3, 433) and gives his reasons for believing that the experiments of Ercolini (3, 433) are faulty. *W. D. B.*

Do rarefied gases show electrolytic conductivity? *E. Bouty. Comptes rendus*, 129, *152* (*1899*). — A Crookes tube paraffined on the outside shows only a slight change of capacity when introduced as an isolated conductor between the plates of a condenser. A Geissler tube behaves in the same way until the potential difference exceeds a certain value, at which point there is a large increase in capacity. From this, the author concludes that one cannot speak of free ions in a rarefied gas under normal conditions. *W. D. B.*

On the discharge of electricity through heated rarefied gases. *J. Stark. Wied. Ann.* 68, *919, 931, 942* (*1899*). — In the first of the three communications the author studies the effect of a charge of electricity brought near the filament of an incandescent lamp when cold and when heated by the passage of an electric current. He finds that the absolute value of the induced charge of the carbon filament is greatly reduced by heating both for positive as well as negative electricity, but much greater for the latter than the former. By fastening a metal electrode in the lamp, and connecting through a galvanometer with one pole of the exciting current, a current is shown on the galvanometer. This current the author calls the "gas current". He makes a study of the effect of an induced charge on this gas current and speculates on the cause for a unipolar conductivity. The second paper treats of the properties of the "gas currents". The third paper takes into consideration the current found to pass between two metal electrodes placed in the hot gas in a flowing lamp. Such "bipolar gas currents", the author finds, increase at first slowly as the gas is heated and finally very rapidly. The strength of the gas current increases for a long time with the E. M. F. and is nearly proportional to it. *H. T. B.*

On the discharge of electrified substances, and the formation of ozone. *P.*

Villard. Comptes rendus, 130, *125* (*1900*).—It is shown that there is experimental evidence for assuming that incandescent substances give off cathode rays of low voltage. This hypothesis would bring under one head a number of what are now isolated phenomena. *W. D. B.*

New investigations on argon and its compounds. *M. Berthelot. Comptes rendus*, 129, *71* (*1899*).—Under the influence of the silent discharge, argon is absorbed to a certain extent by carbon bisulfid and by substances containing the benzene ring. None of the compounds were obtained pure for analysis. *W. D. B.*

On the combination of carbon bisulfid with hydrogen and with nitrogen. *M. Berthelot. Comptes rendus*, 129, *133* (*1899*).—Carbon bisulfid and hydrogen combine under the influence of the silent discharge to form a compound $C_2H_2S_4$ if the voltage be high enough; otherwise the polymerization of the carbon bisulfid is the chief reaction. The experiments with nitrogen and with argon are still in the rudimentary stage. *W. D. B.*

Note on the combination of nitrogen with oxygen. *M. Berthelot. Comptes rendus*, 129, *137* (*1899*).—Under the influence of the electric spark it appears that N_2O_3 is formed as an intermediate step in the formation of NO_2, even when an excess of oxygen is present. *W. D. B.*

Action of argon and of nitrogen on mercury alkyls. *M. Berthelot. Comptes rendus*, 129, *378* (*1899*).—Mercury diphenyl absorbs argon under the influence of the discharge. Mercury dimethyl absorbs nitrogen, but not argon. *W. D. B.*

On radio-activity caused by Becquerel rays. *P. and S. Curie. Comptes rendus*, 129, *717* (*1899*).—It has been found that the rays emitted by polonium and radium have the power of making inactive substances temporarily active and that this induced radio-activity may persist for a very considerable length of time. *W. D. B.*

On the spectrum of radium. *E. Demarçay. Comptes rendus*, 129, *716* (*1899*).—The evidence seems to be fairly conclusive that radium has a spectrum of its own, quite distinct from that of barium. *W. D. B*

Chemical action of the Becquerel rays. *P. and S. Curie. Comptes rendus*, 129, *823* (*1899*).—The rays given off by radium convert oxygen into ozone and decompose barium platinocyanid slowly. *W. D. B.*

Investigations on the phenomena of phosphorescence caused by the radium rays. *H. Becquerel. Comptes rendus*, 129, *912* (*1899*).—The rays from radium cause phosphorescence in substances which phosphoresce under the influence of ultra-violet rays. *W. D. B.*

Effect of a magnetic field on the radiation from radio-active substances. *H. Becquerel. Comptes rendus*, 129, *996*, *1205* (*1899*).—When radium is brought into an inhomogeneous magnetic field, such as that of an electromagnet, the radiation concentrates at the poles; but this is not the case with polonium. *W. D. B.*

Action of the magnetic field on the Becquerel rays. *P. Curie. Comptes rendus,* 130, *73* (*1900*). — If the magnetic field be placed close to the radium, a part only of the rays are deflected; if placed at a distance, all of them. This seems to imply that there are certain rays which cannot be deflected and which, in this state, at any rate, only extend a short distance from the surface. None of the radiations from polonium can be deflected, and they seem to be limited in space. *W. D. B.*

On the penetration of the Becquerel rays which are not deflected by the magnetic field. *S. Curie. Comptes rendus,* 130, *76* (*1900*). — By conductivity methods it is shown that the rays which are not deflected are absorbed the more readily the greater the thickness of matter through which they have passed, while the reverse is true for the other rays. *W. D. B.*

Contribution to the study of radiation of radium. *H. Becquerel. Comptes rendus,* 130, *206, 372* (*1900*). — Further study of the action of a magnetic field. *W. D. B.*

Further experiments with Becquerel rays. *J. Elster and H. Geitel. Wied. Ann.* 69, *83* (*1899*). — The authors suggest as a possible source of the luminous energy, the change of the atom from a less to a more stable position. If this is the case, the radio-activity must disappear with time. Experiments made by the authors tended to show that Becquerel rays are not affected by a magnetic field. *W. D. B.*

On the behavior of radio-active barium and on polonium. *F. Giesel. Wied. Ann.* 69, *91* (*1899*). — Freshly crystallized barium salts containing radium show only a slight activity. This increases for several weeks, finally reaching a maximum and then remaining constant. A concentrated aqueous solution is at first almost as active as a solid salt; but the radio-activity gradually decreases to zero. On the other hand, some active polonium compounds, obtained by precipitation with hydrogen sulfid, gradually lost their activity. This could be brought back by dissolving and reprecipitating. *W. D. B.*

On the deflection of Becquerel rays in a magnetic field. *F. Giesel. Wied. Ann.* 69, *834* (*1899*). — The author finds that the rays from radium and from polonium can be deflected by a magnetic field. *W. D. B.*

On the spectra of oscillating discharges. *H. A. Hemsalech. Comptes rendus,* 129, *285* (*1899*). — By inserting a self-induction in the outer circuit of a Leyden jar, it is possible to eliminate nearly all the lines due to the air. Some of the metallic lines are strengthened and some weakened. The author shows that this interesting result is probably a question of the temperature of the spark. *W. D. B.*

Studies on reversible photochemical processes. *R. Luther. Zeit. phys. Chem.* 30, *628* (*1899*). — Sunlight decomposes silver chlorid with evolution of chlorin, and chlorin regenerates, or bleaches, blackened silver chlorid. If silver chlorid suspended in aqueous solution be exposed to sunlight, there must be an equilibrium concentration of chlorin in the solution, which will be a function of the intensity of the light. The author has determined these equilibrium concentrations for silver chlorid and silver bromid. He has also developed a theory that the difference of chemical potential must be proportional to the difference of potential of the radiant energy or that the difference of the logarithms of the chlorin or bromin concentrations must be proportional to the difference in intensity of the light. This is not the case experimentally.

Incidentally, the author shows the existence of Ag_2Cl and of Ag_2Br by electrometric methods. *W. D. B.*

On the stereochemistry of nitrogen. *J. A. Le Bel. Comples rendus*, 129, *548* (*1899*). — Full directions are given for preparing the optically active substituted ammonium compounds first made by the author in 1891, the existence of which has since been disputed. *W. D. B.*

On the rotatory power of active valerianic acid. *A. Guye and E. Aston. Comples rendus*, 130, *585* (*1900*). — The rotatory power of amyl alcohol as liquid is different from the value as vapor, whereas the two values are nearly the same for valerianic acid. The explanation is that liquid amyl alcohol is markedly polymerized while the vapor is not. In the case of valerianic acid both liquid and vapor are polymerized. This case is interesting as showing that it is not safe to assume that a liquid is normal because its rotatory power is very nearly the same as that of its vapor. *W. D. B.*

On some previously unnoticed lines in the ultra-red portion of the argon spectrum. *R. Nasini, F. Anderlini, and R. Salvadori. Rend. Accad. Lincei*, (*5*) 8, *II*, *269* (*1899*); *Gazz. chim. Ital.* 30, *I*, *189* (*1900*). — By photographing the spectrum of gas from one of the Vesuvian *fumaroles*, the authors have discovered six new argon lines in the ultra-red, the wave-lengths being 798.0, 803.0, 814.0, 832.0, 845.0, and 857.5. *W. D. B.*

Refaction indices of pure water and normal salt solutions. *C. Bender. Wied. Ann.* 69, *676* (*1899*). — A continuation of the author's work (4, 64) on the refractive index of water between 10° and 40° C. With slightly modified apparatus he studies the hydrogen lines H_α, H_β, and H_γ for pure air-free water between 40° and 70° C, and gives simple parabolic formulæ similar to the ones given in the first paper. *H. T. B.*

On the double-vessel refractometer, and investigations of certain solutions with it. *W. Hallwachs. Wied. Ann.* 68, *1* (*1899*). — The author has now studied in detail the differential method previously outlined by him, Wied Ann. 50, 577 (1893). The sources of error are discussed. The lower limit for $n - M_0$ is 3×10^{-4} with an accuracy of one-half percent at this point. In the study of solutions, it was found that a change of dissociation has no measurable effect on the index of refraction, except perhaps in the case of hydrogen as ion. The conclusions of Le Blanc and Rohland are shown to be based on faulty experimental work. *W. D. B.*

Crystallography, Capillarity and Viscosity

On the non-existence of the hexagonal system. *F. Wallerant. Comples rendus*, 130, *275* (*1900*). — The author claims that "the hexagonal system does not exist in nature and that the system has only a theoretical importance." Crystals which have hitherto been classed in this system are really cubical. *W. D. B.*

On the surface-tension of some organic liquids. *P. Dutoit and L. Friderich. Comptes rendus,* 130, *327* (*1900.*). — The authors conclude that the value of *k* in the formula of Ramsay and Shields is not the same for all normal liquids. Thus they find 2.12 for substances with one benzene nucleus, 2.30 for substances with two benzene nuclei, and 2.35-2.50 for the anilins. The authors believe therefore that liquids should be considered normal when the coefficient *k* is independent of the temperature, and abnormal when it is not. This would exclude the possibility for the present of calculating the degree of association.

W. D. B.

Investigation of surface-tension between liquid phases with the cohesion balance. *A. Pockles. Wied. Ann.* 67, *668* (*1899*). — The chief result of the investigation is that in some cases the surface-tension is a function of the thickness of the second liquid film.

W. D. B.

On the viscosity of gases and the change with the temperature. *P. Breitenbach. Wied. Ann.* 67, *803* (*1899*). — The viscosity coefficient increases proportionally to some power of the temperature, the exponential factor varying from 0.6 to 1.0 for different gases and decreasing slightly with increasing temperature for the same gas. Even this carefully modified approximation does not hold at low temperatures. In a mixture of gases the viscosity coefficient is not an additive function.

W. D. B.

THE ALLOTROPIC FORMS OF SELENIUM[1]

BY A. P. SAUNDERS

INDEX

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[1] The change to *selenion* advocated in Watts' Dictionary because of the pseudo-metallic character of the element seems unnecessary; the statement made there to the effect that Berzelius so named it, is incorrect. Berzelius called it *selenium* while expressly recognizing it as pseudo-metallic, between sulphur and tellurium.

I. INTRODUCTION

The present investigation was taken up for the purpose of establishing the general relationships of the allotropic forms of selenium, and of determining their limits of stability. The descriptions commonly given are confusing because no systematic study of the subject has ever been made. The only available data which could lead to any conclusions are those relating to specific gravities, but these have often been determined without sufficient attention being paid to the methods by which the materials were prepared, or the conditions under which accurate results can be expected. Since none of the textbooks give any adequate review of the literature dealing with this element, it is proposed to gather together here a few notes on the principal memoirs which have appeared since the discovery of selenium in 1818. This review will be strictly limited to those which deal with the properties of the element itself, neglecting those devoted to its compounds.

For convenience in discussing the earlier memoirs, the conclusions to which the present investigation has led, are given below, after the list of references to the literature. Following these there comes a description of the method of purification used, and then a discussion of the results previously recorded in the literature and those which the present experiments have brought out; these experiments include specific gravity determinations, dilatometric measurements, experiments on the behavior of selenium in liquids and miscellaneous observations; here follow also sections on the heat of transformation, specific heat, conductivity, etc. Finally, there will be found a section devoted to a description of the general physical properties, such as the atomic weight, vapor density, etc., which are only inserted here for the sake of completeness.

II. LIST OF REFERENCES[1]

1818. Berzelius. Schweigg. J. 23, 309–344, 430–484. Discovery; separation; character; compounds; atomic weight.

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[1] It should be noted that I have used the abbreviation "Ann." for both the Annales de chimie et de physique, and Liebig's Annalen. Since the series number always accompanies references to the former, no ambiguity is possible.

1826. Seebeck. Pogg. 6, 155. Electrification of vitreous selenium.
— Berzelius. Pogg. 7, 242. Purification.
— Berzelius. Pogg. 8, 21. Atomic weight.
1827. Mitscherlich and Nitzsch. Pogg. 9, 627–630. Selenic acid, and salts.
— Magnus. Pogg. 10, 491. Solubility in sulphuric acid.
1828. Fischer. Pogg. 12, 153–155. Solubility in sulphuric acid.
— Magnus. Pogg. 14, 328. Solubility in sulphuric acid.
1829. Fischer. Pogg. 16, 121. Solubility in sulphuric acid.
1830. Magnus. Pogg. 20, 165–166. Separation from compounds.
1831. Rose. Pogg. 21, 431. Sulphur, selenium, tellurium.
1839. Knox. Trans. Roy. Irish. Acad. 19, 149 (1843); or Phil. Mag. [3] 16, 185. Conductivity.
1840. Regnault. Ann. [2] 73, 51. Specific heat.
— Fröbel. Pogg. 49, 590–591. Crystal form of the metallic modification.
1845. Riess. Pogg. 64, 50. Electrification of vitreous selenium.
1847. Sacc. Ann. [3] 21, 119–126. Atomic weight.
1848. Schaffgotsch. J. pr. Chem. 43, 308–309. Specific gravities.
1849. Erdmann and Marchand. J. pr. Chem. 55, 202 (1852). Atomic weight.
1851. Hittorf. Pogg. 84, 214–220. Melting-point of the metallic form, 217°. Transformation from vitreous to metallic causes evolution of heat. Specific gravity of metallic form. Vitreous selenium a non-conductor. Metallic selenium a conductor.
1853. Schaffgotsch. Pogg. 90, 66–82. Specific gravities.
1855. Mitscherlich. Berl. Akad. 409–416, or J. pr. Chem. 66, 257–265, or Ann. [3] 46, 301–313. Description of the red crystalline form, its crystallography, density, melting-point; transformation of amorphous and vitreous selenium in carbon disulphide.
1856. Regnault. Ann. [3] 46, 281–301, or Pogg. 98, 418–434. Specific heat; transformation; general properties; heat of transition.
1857. Oppenheim. J. pr. Chem. 71, 279–282. Separation from tellurium by potassium cyanide.
— Böttger. J. pr. Chem. 71, 512. Decomposition of selenide solutions.
1859. Dumas. Ann. [3] 55, 186–187. Atomic weight.
— Deville and Troost. C. r. 49, 239. Vapor density.
1860. Uelsmann. Ann. 116, 122. Various compounds.
1863. Deville and Troost. C. r. 56, 891. Vapor density.
— Werther. J. pr. Chem 88, 180–181. Spectrum.
1865. Böttger. J. pr. Chem. 94, 439–440. Separation by dissolving in sodium sulphite solution.
— Neumann. Pogg. 126, 123. Specific heat and specific gravity of the metallic form.
— Plücker and Hittorf. Phil. Trans. 155, 1–29. Spectrum.
1866. Schneider. Pogg. 128, 327–334. Solubility in selenious bromide; preparation of that substance.
1868. Bettendorf and Wüllner. Pogg. 133, 293. Specific heat of vitreous and metallic selenium. Specific gravity of the metallic form.
— Quincke. Pogg. 135, 629. Capillarity constant.

1869. Fizeau. C. r. 68, 1125. Coefficient of expansion.
— Schultz-Sellack. Berl. Akad. Ber. 745, or Pogg. 139, 182. Diathermancy.
— Rathke. J. pr. Chem. 108, 235–254 and 321–356, or, somewhat condensed, Ann. 152, 181–220. Analogies between selenium and sulphur. Various selenium compounds.
1871. Sirks. Pogg. 143, 429–439. Refraction and dispersion of amorphous selenium.
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1873. Petersson. B. 6, 1466–1477. Separation by means of potassium cyanide.
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1876. Pettersson and Ekman. B. 9, 1210–1212. Atomic weight.
— Draper and Moss. Ch. N. 33, 1. Conductivity and light effect.
— Moss. Ch. N. 33, 203. Effect of mercury on conductivity of selenium.
— Adams. Pr. Roy. Soc. 24, 163–164, or Pogg. 159, 629–631. Conductivity and light effect.
— Siemens. Pogg. 159, 117–141, or Berl. Akad. Effect of light and heat on the conductivity of selenium.
— Adams and Day. Pr. Roy. Soc. 25, 113–117. Conductivity and light effect.
1877. Braun. Wied. 1, 95. Conductivity and light effect.
— Forssmann. Wied. 2, 512–521. Conductivity and light effect.
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III. THE FORMS OF SELENIUM (IN BRIEF)

Selenium exists in three distinct forms:

1. Liquid (including vitreous, amorphous, and soluble selenium).
2. Crystalline red (including perhaps two closely allied forms).
3. Crystalline gray or metallic.

1. Liquid selenium has the properties of an ordinary liquid at temperatures above 220°. Below that it becomes gradually more and more viscous, remains soft down to about 60°, and at 30°–40° gets quite hard and brittle. In this form it is ordinarily known as vitreous selenium, from its conchoidal and brilliant fracture, and it is by that name that it will be called in the following pages. Its streak is red and it yields on powdering at first a gray powder, but if rubbed up very fine this becomes red and cannot then be distinguished from the form known as red powdery, or amorphous selenium, which I shall designate by the latter name. Amorphous selenium is the state in which the element separates from solutions of selenious acid on reduction; it forms, when dry, an impalpable powder without any trace of crystallinity. When warmed to 40°–50° it darkens in color and coagulates to a soft mass, which, when cooled, becomes hard and brittle again, assuming somewhat the fracture of the vitreous form. Amorphous selenium shows all the properties of the vitreous form, making due allowance for the difference in the state of aggregation, — the only difference which separates them.

Liquid selenium, whether amorphous or vitreous, is soluble to a slight extent in carbon disulphide.

Amorphous selenium, when freshly precipitated, under certain conditions, from selenious acid solutions, is soluble in water, and in this state it is known as soluble selenium. The property is lost with lapse of time.

2. The red crystalline form separates from solutions in carbon disulphide or may be obtained by simply allowing the amorphous or vitreous form to stand in contact with that or some other solvent at ordinary temperatures. It is probable that it has two different crystal habits, both belonging to the same system, and both soluble in carbon disulphide; there may be a slight difference of stability between these two; there are indications of an instable melting-point at about 170°.

3. Gray crystalline or metallic selenium as I propose to call it, is obtained from any of the above forms at higher temperatures; in presence of certain liquids the change takes place even at ordinary temperatures. The ease with which the transformation can be effected depends upon several factors, but the same form always results. This is the stable form of selenium, at all temperatures from the ordinary temperature to the melting-point, 217° C. The other two forms are instable, the red crystalline one representing an intermediate stage between liquid and metallic selenium. It has not proved possible to effect a reverse transformation from the metallic into any other form below 217°, hence there is no real transition point in the physical property curves of the element.

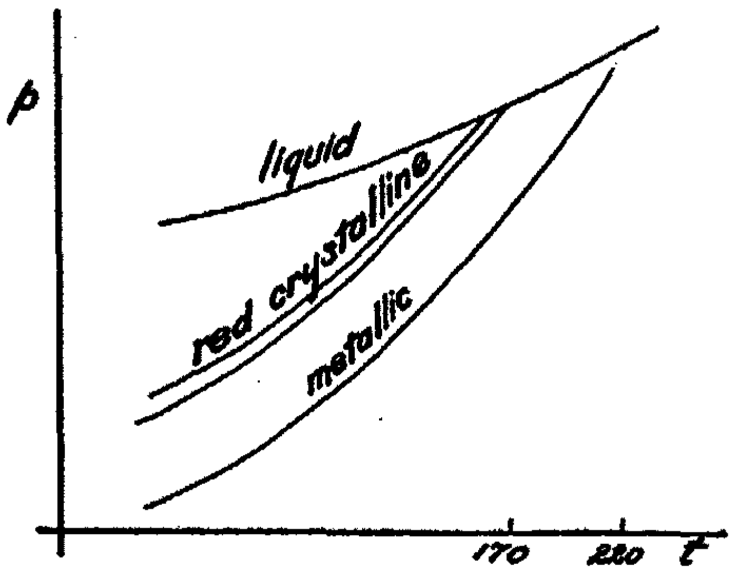

Fig. 1

Thus the curves representing the changes in vapor-pressure for changes in temperature should be, in their general character, somewhat as shown in the accompanying drawing (Fig. 1).

IV. PURIFICATION OF THE MATERIAL

It was not essential for the present investigation that the last traces of impurity should be removed; hence no attempt was made to prepare absolutely pure selenium. The substance in its original form contained a considerable quantity of sulphur and a very little tellurium as impurities. The method used was to dissolve by heating in concentrated sulphuric acid, thus oxidizing the selenium to selenious acid, and then to precipitate by means of sulphur dioxide. Before precipitating, the sulphuric acid solution was diluted with water, and if necessary, filtered.

Divers and Shimosé (1884) found that this method of purification was effective in removing the tellurium which does not come down under these conditions but may afterwards be precipitated by the addition of hydrochloric acid.

After reduction, vigorous shaking is necessary to bring the material together, and it should then be washed until the washings show no further acidity. If the red selenium be then separated on the filter, it will be found very difficult to dry; standing for weeks in a desiccator over sulphuric acid will not free it from water; it is therefore better to make a final washing with alcohol, then filter and dry in the air on a porous porcelain plate. One gram of the material thus purified, when dissolved in nitric acid and diluted gave no appreciable indications of the presence of tellurium, and a test for sulphur showed that this element also was present in only very small quantity.

V. THE PROPERTIES AND TRANSFORMATIONS OF THE DIFFERENT FORMS OF SELENIUM

1. The vitreous modification

The form in which the element comes into commerce is the one known as vitreous, from its brilliant conchoidal fracture. The commercial material in former years consisted of medallions bearing the image of Berzelius, the discoverer of the element, but it is now almost always supplied in rods. Its color in the mass is black, but thin fragments are translucent and display a deep ruby-red color, and when very finely powdered, the powder is red. When heated, it begins to soften at about 50°, and if the heating is extremely rapid, it is possible to raise the temperature to 220° without causing any transformation into a denser form; at this temperature it is distinctly liquid, though still viscous; it does not attain a state of thin fluidity below about 250°. This has led to a misleading statement in many of the textbooks, the responsibility for which rests with Sacc (1847), to the effect that, while the gray crystalline or metallic variety melts sharply at 217°, the vitreous form only becomes really liquid at 240°–250°. The fact of course is that the liquid obtained at 217° is the same from whichever source, but it possesses at that temperature, a moderately high viscosity. When melted selenium is cooled down, the vitreous form is always obtained, unless the cooling is conducted very slowly, in which case it may go over to the more stable metallic form.

Berzelius (1818) remarks that the vitreous form is semi-fluid at 100°, completely so a few degrees higher; probably in his experiment the transformation into the metallic form set in at about the time that the temperature had attained 100°; this change sets free so large a quantity of heat that the mass may very well have assumed for a few moments a state of thin fluidity.

If vitreous selenium be slowly heated and a thermometer placed in the mass, it is found (Regnault, 1856) that when the temperature has attained a point about 96°–97°, there is a sudden rise in the temperature, amounting under favorable circumstances to as much as 150°; the mass becomes completely fluid and after a few moments hardens again. The substance thus formed is found, when examined, to possess quite different properties from the original vitreous selenium. This is, in fact, the gray crystalline form, appropriately called by Regnault metallic selenium.

This transformation was studied by Hittorf (1851), later by Regnault and many others. Regnault's observation that the change begins at 96°–97° has led to the belief that there is something significant in these temperatures. Such is not the case. The fact is that vitreous selenium probably goes over into the metallic form at all temperatures under 217°, but the change, in the absence of solvents, does not possess a measurable velocity below about 90°. Indeed Regnault states that it may be kept for hours at 90° without any change occurring. This is probably true, in general, when selenium is heated by itself; nevertheless Hittorf states that the change occurs anywhere between 80° and 217°, and Rammelsberg (1876) gives 90° as the limit of stability. At 95° or any higher temperature, until we approach the melting-point, the change goes on rapidly. Hittorf made some experiments to determine the point of maximum velocity, and placed it at about 125°.

Positive evidence was still wanting, to show whether the change was really a reversible or an irreversible one, i. e., to determine whether vitreous selenium is really unstable at all points below 217°, or whether it has at lower temperatures a region of stability. The idea of a transition point has gained a hold on the minds of some, through a remarkable experiment of Lehmann, which we shall now consider. Thus Tammann (1897) has been led to consider this an example of a substance having a second melting-point, analogous to the case of chloroform as reported by Pictet.[1] Further, Le Chatelier in a more recent article[2] expresses himself in these words: "Selenium is only stable in the crystalline state above 60° and below 214°. Outside of these extreme limits of temperature, the amorphous modification (vitreous, liquid) alone is stable."

The observation of Lehmann upon which these statements are based, was made with the microscope and is reported by him as follows:[3]

" When melted under a cover-glass, selenium appears as a clear red transparent liquid; on further warming, the liquid gets darker and black points make their appearance here and there; these increase in size and assume the aspect of spherical aggregates (sphärolithische Aggregationen) of the insoluble gray

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[1] Zeit. phys. Chem. 16, 422 (1895).
[2] Comptes rendus, 129, 282 (1899).
[3] Molekularphysik, I, 712.

modification. ... The crystals soon fill the whole field, and, on still further heating, the mass melts to a dark, almost opaque liquid. . On cooling down slowly, the spherical crystals of the gray modification appear at first, and then, as they grow steadily smaller, the color of the liquid becomes less intense, and we obtain finally the original clear red liquid. If the cooling is rapid, the crystals of the gray modification do not appear, but the liquid passes gradually from dark red to light red. The same behavior is shown on rapid warming; here also the black crystals may appear momentarily and disappear again, but sometimes the transition is direct from the red condition into the more deeply colored one. The increased absorption of light on heating and the reverse change on cooling, point to a chemical change in the liquid such that it is to be regarded at higher temperatures as partially a solution of the gray modification.

On attempting later to reproduce the above inversion (Rückgängigwerden der Entglasung) it did not prove possible to do so; perhaps because of greater or less impurity of the selenium, perhaps because the conditions were not favorable for the production of the gray (light-sensitive, less conducting) modification." All my attempts to repeat this observation of Lehmann's also failed. I have not been able to find under the microscope anything abnormal in the behavior of the element. Lehmann's observation must therefore remain for the present unexplained; possibly local heating or some other experimental irregularity may have been the cause of the appearance and subsequent disappearance at lower temperatures, of the crystals.

A better method of approaching this problem is afforded by measurements with the dilatometer, and the following section is devoted to an account of such experiments.

Dilatometer Measurements

The experiment of Lehmann, to which reference is made above, indicated the possibility of a real transition point in the change from vitreous to metallic selenium. Dilatometric measurements being the most satisfactory means of establishing such a point, the present study was begun with the dilatometer. The difficulties met with, which are discussed later on, had their source in the fact that it was necessary to work over a range of more than 200°, and it was not easy to find a liquid which answered the purpose. Several were tried: aniline, quinoline, glycerine, and solid and liquid paraffin.

For those determinations which were made with solid paraffin, it was necessary to surround the stem of the dilatometer with a steam jacket, and also to enclose that part of it which passed through the lower stopper of the jacket, in copper tubing, to prevent the solidification of the paraffin in the capillary.

Even when liquid paraffin is used, the steam jacket is of value because, without it, the high viscosity of the paraffin at lower temperatures renders it difficult to obtain concordant results, where the bulb is subjected to rapid changes through a wide range of temperature.

For the sunlight experiments, a bath of glycerine or high-boiling paraffin was used; for the others, a bath of oil. The Reichert gas regulator proved of service in maintaining a constant temperature within a couple of degrees, when it was desired to keep the bath for some time at a fixed point. The stirring was done by means of an electric motor; what is known as the Ajax motor proved most efficient. The dilatometer tube was always sealed; hence the pressure was generally higher than one atmosphere for the upper ranges of temperature. The recorded experiments are given under their original numbers, so that the series as given here is not complete.

Dilatometer Experiments

Experiment 1. Amorphous selenium in aniline. The following readings were obtained:

Temp.	Scale	Time	Temp.	Scale	Time
20.1°	9	12 : 30	21°	10.7	9 : 25
—	9	12 : 45	70	125.2	10 : 40
29.9	32.5	1 : 15	—	123.8	10 : 45
—	32.5	2 : 45	—	120.5	10 : 52
40.2	56.7	3 : 20	—	118.5	10 : 56
—	56.7	3 : 50	65.5	104.8	11 : 15
49.8	79	4 : 20	—	104.3	11 : 35
—	79	4 : 50	—	104.2	11 : 56
60.1	103.2	5 : 10	59.9	90.8	12 : 15
—	103.2	5 : 35	—	90.8	12 : 40

The material was then slowly cooled to room temperature.

23.2°	3.2	2 : 28	71°	116.8	9 : 42
23.1	3.0	2 : 40	—	117.0	11 : 00
22.5	2.0	4 : 00	80.2	138.3	11 : 17
69.6	113.6	4 : 15	—	138.3	11 : 31
—	113.7	4 : 33	97	177.3	12 : 22
70.8	116.5	4 : 36	—	177.3	12 : 37
—	116.3	5 : 00			

The first group of values shows that amorphous selenium in aniline shows no immediate change in volume when heated to 60°. (Later experiments have shown that there is a change when amorphous selenium remains in contact with aniline, even at ordinary temperatures; but this goes on comparatively slowly). The second group shows that at 70° a change sets in, which continues, though slowly, when the temperature is lowered to 65°; the apparent checking of the reaction at 60° was probably due to the fact that all the selenium was already transformed. It is important to notice that there was no sign of a tendency to return to the original volume when the temperature was maintained for twenty-five minutes at 60° and then slowly lowered to the temperature of the room. The remaining values show that no further change goes on up to 97°; the slight variations in tenths of a millimeter on the scale are not to be regarded as significant. In this experiment it was noticed that at 40° the selenium had shrunk together to about half of its original volume, and when the temperature had reached 50° it had become almost black and formed a small mass in the bottom of the bulb.

Experiment 4. Amorphous selenium in aniline, using a larger quantity of selenium than in exp. 1. In this experiment, as in many which follow, the rise in temperature of the bath was slow and continuous, and readings were taken at intervals; not all of these are recorded here, but enough to make it possible to reconstruct the expansion curve; where any change was perceptible, the temperature was held constant for a time at that point. The selenium used in this experiment was first heated to 50° to facilitate the liberation of air bubbles which adhere to the powder.

Temp.	Scale	Time	Temp.	Scale	Time
19.8°	10.3	12 : 20	—	90.3	3 : 03
60.1	97.0	12 : 40	Transferred to cold water		
—	97.2	12 : 43	20.2	3	3 : 09
60	91	3 : 00	—	3	3 : 40
After standing over night					
17°	—2	9 : 35	66°	89	12 : 05
28	18	9 : 50	—	64.5	12 : 50
35	35	10 : 02	—	61	3 : 00
43	52	10 : 15	69	67	3 : 05
48	63	11 : 22	79	87.5	3 : 23
60	87.5	11 : 48	90	109.5	3 : 45
66	95.5	11 : 58	100	129	4 : 15

The dilatometer was then cooled down, and in a subsequent experiment lasting about four hours the temperature was slowly raised from 72° to 202° without any irregularity in the expansion curve being observed.

In experiment 4, the contraction took place in two different stages separated by a period of cooling and then a slow rise in which the temperature was maintained for one and one-half hours between 43° and 60° without any return toward the original readings. This confirms the evidence of exp. 1, showing that when both forms of the substance are present, the change is still only capable of going one way, i. e., is irreversible. In a later experiment this dilatometer was heated in direct sunlight during forty-five minutes from 113° to 162°; the readings give no indication of any change in the selenium. It may be as well to state here what is later established, that the denser form obtained in all of these dilatometric experiments is metallic selenium of density 4.8.

It was desirable after completing these experiments to heat the dilatometer up to 220° in order to transform the selenium again into the liquid modification, without being under the necessity of removing it from the bulb. It did not prove practicable to do so in aniline on account of the evolution of gas, which begins in that liquid at temperatures varying from 160° upwards, according to the pressure within the tube. Aniline was therefore abandoned, and a few experiments were tried with glycerine; the same difficulty was encountered with this liquid too; nevertheless several sets of observations were made, up to about 200°, with the result that the transformation of vitreous selenium was found to begin at about 75°, no further change being observable up to 200°, nor was there any sign of a reverse transformation when the tube stood at 25°. The experiments of Siemens and others on the conductivity of selenium indicated the possibility of some change taking place in sunlight at 160° or above, but although the tube which contained metallic selenium was kept for half an hour under a burning-glass, in a bath whose temperature varied between 156° and 172°, no change was found to occur.

Some experiments were then made in quinoline. Starting with metallic selenium, the dilatometer was heated in the dark for five hours between 154° and 196° without any indication of a change at any point. Subsequent heating for three hours between 150° and 200° only confirmed this result. The tube was then brought into direct sunlight, placed under a burning-glass, and heated, on different days, for one and one-half hours between 150° and 180°, for one and one-half hours from 190° to 195°, and for one-half hour from 198° to 201°; the readings are, within the limits of experimental error, identical with the original observations when the heating was carried on in the dark. These observations make it extremely improbable that metallic selenium suffers any change either in the dark or in direct sunlight, when heated to temperatures between 150° and 200°. It does not of necessity follow that the element will behave in the same way when heated in a liquid capable of dissolving it, as it will when heated by itself; on the other hand, the probability is that any change which goes on in the substance taken by itself, which leads to the production of a more stable form, will take place only the more readily in presence of a solvent. Thus, it will be shown later on that amorphous selenium, which is capable of existing by itself for an indefinite time without change, at ordinary temperatures, goes over rapidly, in the presence of pyridine and certain other liquids, to the metallic form.

The same difficulties which had been met with in working with aniline and glycerine were once more encountered with quinoline when the temperature was raised above 200°. It was supposed at first that all of these reactions were with the liquids themselves, but it seems more probable from later observations that the difficulty is due to small quantities of water which adhere to the selenium from the method of purification. The dilatometers when opened always had the odor of selenium hydride. Meanwhile it had been found that solid paraffin promised to give better results, and this material was then employed for several sets of observations. It was thus rendered possible to work freely between 20° and 230°, although the results of successive transformations into the metallic form did not always lead back exactly to the same reading, on account of the gradual accumulation, in the selenium, of gas bubbles, which, under the prevailing high pressures, did not free themselves from the mass. This difficulty was obviated later by opening the tube from time to time to let the bubbles escape.

Experiment 23. Metallic selenium heated in paraffin from 60° to 210° shows no irregularity. When the temperature is raised to about 218°, the selenium begins to melt and expands; at 220° the melting was complete in half an hour, and on cooling, the vitreous form was produced. The readings are as follows:

Temp.	Scale	Time
60°	30	11 : 55
172	257	12 : 10
200	315	
210	336	
218	360	12 : 15 (fusion begun)
222	412.5	12 : 49 (fusion complete)
the tube was then cooled rapidly		
57.5°	57	12 : 55

The dilatometer was then placed in a bath at 160°, whose temperature was rapidly rising. The level in the capillary rose at first, then rapidly fell, showing a sudden transformation from the vitreous to the metallic modification. The tube then stood in direct sunlight for an hour, at about 200°. At the end of the time, the reading was 311, almost identical with the above. Thereupon the temperature was raised to about 228°, and the material completely fused, after which the bath temperature was brought down to 200°, in order to determine what change takes place when melted selenium is maintained at that temperature. The readings are as follows:

Temp.	Scale	Time	Temp.	Scale	Time
225°	418	3 : 42	200°	351	4 : 24
199	367	3 : 45	—	344	4 : 33
199	363		—	339	4 : 40
198	359	3 : 47	—	335	4 : 48
198	357.5	3 : 49	—	330	4 : 55
198	357.5	3 : 52	—	325	5 : 03
197.5	356	4 : 01	—	322	5 : 15
199	356.5	4 : 10	—	320	5 : 25
199.5	355.5	4 : 15	—	320	5 : 36
200	353.5	4 : 20	—	319	5 : 46

The dilatometer was then cooled to 65° where the scale reading was 30. This reading, like the final reading at 200° is somewhat higher than that previously obtained. A few small bubbles of gas were observed in the bulb at the end of the experiment and it is to them, no doubt, that the variations are to be attributed. This experiment in itself would not be conclusive without the confirmation of later observations; the values are given in detail to indicate the rate at which the change goes on at 200°. The falling level in the first readings at 199° is not due to a change in the selenium, but to the lag of the instrument which does not adjust itself at once to the changed bath temperature; a closer inspection shows that the transformation of the selenium did not set in until about half an hour later and was complete about an hour after it commenced. The rate is at first very slow, then increases and remains almost constant until near the end, when it is much retarded.

Experiment 24. The same dilatometer was again heated slowly up to 217°, the following readings being obtained:

Temp.	Scale	Time	Temp.	Scale	Time
117°	132	2 : 56′	160°	225	3 : 24
130	161	3 : 02	172	250	3 : 39
140	182	3 : 14	182	271	3 : 49
150	203	3 : 18	201	311	4 : 15

The tube was then cooled down:

169°	248	4 : 27
155	219	4 : 32
120	145	4 : 52

then heated to 225° to effect fusion, after which the following readings were obtained on cooling down:

225°	415	5 : 37	165°	290	5 : 57
185	336	5 : 41	150	257	6 : 01
—	332	5 : 42	130	212	6 : 12
—	332	5 : 50	69	82	6 : 18
180	322	5 : 52			

This shows that melted selenium in paraffin may be cooled down quite slowly without any transformation taking place, for the last of the above readings agrees with that found for the vitreous form in the preceding experiment where the bulb was cooled at once from 220° to 57°. In order that the paraffin might not solidify, the tube was placed over night in water which varied in temperature from 60° to 75°; on the following morning, a reading was taken at 74° and the level was found to be 78, showing that the selenium had suffered contraction but had not gone over entirely to the metallic form. On then raising the temperature, the following readings were made:

Temp.	Scale	Time	Temp.	Scale	Time
74°	78	10 : 50	111°	127	10 : 30
85	100	11 : 02	111.5	125	11 : 50
90	108	11 : 05	148	199	12 : 09
95	118	11 : 09	200	309	12 : 33
105	132	11 : 19	152	205	12 : 49
109	131	11 : 26			

These observations were made in diffused daylight. The experiment still further confirms the statement that metallic selenium undergoes no change in being heated to 200° and that when the temperature is brought back to 150° the reading accords with that obtained with rising temperature.

The indications of a partial change at about 70° followed by no further contraction up to 105° are of interest, and a further experiment was undertaken later on in the hope of being able to repeat these observations. The following is the experiment in question:

Experiment 71. Selenium in solid paraffin. During three hours the temperature was slowly raised from 55° to 97° without any indication of a change; at this point contraction began; but the apparatus being left to itself, the temperature gradually fell during the succeeding four hours, to 73°; the change had then proceeded to a considerable extent; further heating at higher temperatures brought out the fact that below 90° the change, even when it has commenced, goes on very slowly — at 80° it amounted to about three scale divisions in an hour, where the total contraction involved nearly 80 scale divisions — but the drop was continuous and reached a limit after about fourteen hours' heating at temperatures between 80° and 90°. This experiment comes in a later class than the preceding, and was made with a weighed quantity of selenium and a dilatometer whose capillary arm had been previously calibrated. This method of procedure is much to be recommended for cases like the present, since it makes it possible to estimate at any moment, approximately, the density of the material studied.

The final density of the selenium was found in this way to be 4.83. The extreme slowness with which the change goes on at 80° suggests that the observations of exp. 24 may have no special significance at all; the change was probably incomplete and did not proceed rapidly to an end until the temperature was raised above 100°.

On the other hand, the existence of red crystalline forms of selenium, which, according to Muthmann, go over to metallic selenium at 110°–120°, and which have a density of about 4.5, points to the possibility of the occurrence here, exceptionally, of such a form; in that case exp. 71 simply failed to reproduce the red form. It should be said further, that no indication whatever of a change of vitreous selenium into the red crystalline modification was observed in any of the other dilatometer experiments, although such a change is known to go on superficially when vitreous selenium is brought into carbon disulphide at ordinary temperatures.

The following experiments were made with liquid paraffin, unless otherwise stated:

Experiment 26. This determination was made as a further study of the density relations of the form of selenium which is produced when the melted element is cooled to 200° and maintained at that temperature until no further change of volume is observed. A dilatometer containing vitreous selenium was placed in a bath at about 150°; at this temperature the change is immediate and gives rise, as is well known, to the ordinary metallic selenium. The experimental data are as follows:

Temp.	Scale	Time	Temp.	Scale	Time
155°	260	12 : 12	219°	531	12 : 47
160	273	12 : 14	200	478	12 : 54
178	323	12 : 20	—	468	12 : 56
198	380	12 : 25	202	461	1 : 06
210	413	12 : 30	200	450	1 : 11
218	440	12 : 33	—	444	1 : 13
220	460	12 : 35	—	438	1 : 15
221	530	12 : 43			

At this point the temperature was allowed to drop for a few moments to 182°; it was raised again at once:

185°	370	1 : 25
198	386	1 : 31
201	393	1 : 32
196	380	2 : 06

The material was then heated again to fusion, and cooled to 200°:

201°	500	3 : 10	200°	443	3 : 49
199	490	3 : 11	200.5	430	3 : 56
198	485	3 : 13	—	418	4 : 11
199	485	3 : 17	198	398	4 : 17
—	485	3 : 20	—	395	4 : 24
200	479	3 : 28	197	389	4 : 44
—	469	3 : 35	199	393	4 : 54
—	461	3 : 39			

This experiment shows clearly that the form produced at 200° is identical with the original metallic selenium. The slight difference in the readings at 200° before and after fusion, is negligible in comparison with the total change of level involved in the transformation. The heating at 220° to effect fusion was prolonged until there was little or no further change during several minutes, since it was plainly desirable to have the mass of selenium free from crystals of the metallic form; on the other hand, there was no object in refining too far upon this point, since we may say certainly that in the cooling down from 220° to 200° there would always be a small quantity of material deposited from the solution, either in the form of metallic crystals, or perhaps in some other modification if such were capable of existence at that temperature.

Experiment 28. This experiment, which was made with the dilatometer used in exp. 27, was undertaken to determine whether or not there are two substances in the melt when selenium is brought to complete fusion and then allowed to go over partially at 200°. If two forms are present in the liquid state, forming but one phase, then the melting-point will be lowered, and in consequence, at temperatures below but very near 217°, any of the solid form present will melt and the dilatometer level will rise; if such is not the case, it will continue to fall. The readings were as follows:

Temp.	Scale	Time	Temp.	Scale	Time
80°	44	9 : 47	221°	558	12 : 01
100	92	9 : 54	200	497	12 : 06
190	350	10 : 32	201	469	12 : 39
207	398	10 : 50	199.5	447	12 : 48
218	433	11 : 02	214	483	12 : 54
220	530	11 : 29	215	478	1 : 08
—	553	11 : 53	214.5	474	1 : 15

It is plain from these figures that at 215°, under the conditions of the experiment, the contraction continued. The recorded temperatures are uncorrected; on comparing the thermometer used with a standard thermometer calibrated at the Reichsanstalt in Berlin, it was found that the one used in these experiments registered 3° too low at 215°. Since selenium expands on melting, it follows from the theorem of Le Chatelier that the melting-point will be raised by increased pressure; but as the prevailing pressure within the tube was, in this experiment, not above 6 to 8 atmospheres, it is improbable that this would very sensibly affect the melting-point. Reicher[1] found that an increase of 4 atmospheres only raised the inversion point for rhombic and monoclinic sulphur by about 0.2°, whereas the melting-points of various substances — water, naphthalene, etc. — are even less sensitive to pressure changes.[2] It seems most likely in this case that the recorded value 217° is somewhat low and that the melting-point of gray selenium should be placed nearer 220°. At any rate, the experiment shows that liquid selenium continues to go over into the solid form at temperatures lying very near the melting-point, and this renders the existence of a second form in the liquid phase most improbable.

Experiment 29. This determination was conducted with the same dilatometer that was used in exp. 28. Starting from vitreous selenium, the following readings were made:

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[1] Recueil Trav. Pays-Bas, 2, 262 (1884).

[2] Ostwald: Lehrb. I, 1013.

Temp.	Scale	Time	Temp.	Scale	Time
55°	60	2 : 38	191°	418	2 : 49 1/2
80	125	2 : 41	197	419	2 : 50
132	270	2 : 45	202	407	2 : 54
158	350	2 : 47	204	406	3 : 06
172	385	2 : 48	201	396	3 : 57
185	410	2 : 49	195	380	5 : 20

This experiment shows that it is sometimes possible, by rapidly raising the temperature of vitreous selenium, to heat it to about 185° before the transformation begins; but a comparison with the readings in exp. 26 shows that the form produced in this way at 200° is the same as that obtained by any of the other methods used; and furthermore, its density is not changed by heating for two and one-half hours at about 200°.

Experiment 30. A continuation of exp. 29. Starting from vitreous selenium, the temperature was rapidly raised, and in this case attained almost 175° before the transformation began. The subsequent readings are as follows:

Temp.	Scale	Time
175°	390	9 : 39
186	397	9 : 40
195	395	9 : 41
203	405	9 : 47
199	393	11 : 20

This confirms the results of exp. 29.

The tube was next heated to 225° to effect fusion, and then cooled to 125° to observe the nature of the transformation at that point. The readings are:

Temp.	Scale	Time	Temp.	Scale	Time
232°	560	11 : 45	176°	310	12 : 43
125	265	12 : 03	—	311	1 : 01
127	231	12 : 16	198	377	1 : 30
—	177	12 : 32	206	399	1 : 50
—	177	12 : 37			

The transformation at 125° brings the dilatometer back to a reading almost identical with that obtained by interpolation from the results of exp. 28, where the dilatometer contained selenium which had been changed over at 200° and then cooled down.

In the experiments which follow, special care was taken to eliminate water from the system. The paraffin used in all these later experiments was dried by sodium. For drying selenium which has been precipitated out of an aqueous solution of selenious acid, it is by no means sufficient to heat it for an hour or two at 120°, although by this means it goes over to the metallic form, and one would suppose that such a change would be likely to set free all the moisture present; on fusing such a preparation in a tube, however, a very considerable quantity of water is still given off. The material here used was dried by heating to 230° for some time, in an exhausted Λ-shaped tube, containing sulphuric acid in the other arm. By observing these precautions and by occasionally opening the dilatometer tube to permit the escape of the small bubbles which had developed in the bulb, it was possible to get very concordant results. These experiments confirm the earlier ones.

Experiment 32. New dilatometer.[1] Starting from metallic selenium, the following observations were made:

Temp.	Scale	Time	Temp.	Scale	Time
84°	51		223.5°	562	3 : 32
153	243		200	477	3 : 36
196	361	2 : 51	192	428	3 : 46
204	386	3 : 06	198	374	3 : 59
219	430	3 : 12	196	362	4 : 11
228	525	3 : 19			

Here the last reading at 196° accords almost exactly with the first. The material was again fused and then rapidly cooled; on heating up again, the transformation began at about 130° and gave, after coming to rest at 191°, a reading of 355, which accords very closely with the above value of 362 at 196°.

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[1] In the later experiments a side tube was set on, at an angle, to the bulb of the dilatometer. This facilitates the filling and can be sealed off afterwards.

Experiment 36 was made with a new dilatometer. The level at 199° corresponding to the more dense form, was 321 on the scale. After fusion and cooling, it was placed in a bath at 200°; the transformation took place very rapidly and the level came to 322 at 199°, from which there was no further change during five minutes. The material was again fused and cooled, and then placed in a bath of boiling water until the change was almost completed; it was then replaced in a 200° bath where it gave a reading of 314 at 197°. The selenium was again fused and cooled down. This time it was placed in a cold bath whose temperature was then rapidly raised — this being the method by which Siemens prepared his light-sensitive selenium cells. The change began at about 120° and the temperature, after reaching 200°, was maintained for some time at that point; the dilatometer gave a final reading of 321 at 200°. On being transferred to a bath of boiling water, it gave a reading of 36 at 99°. The material was once more fused and then placed directly in the water-bath; the final reading was 44 and as the change proceeds very slowly toward the end, this may reasonably be taken as a trifle too high. Finally the temperature was raised to 200° and then lowered to 80°; all the readings so obtained were found to lie along one line and there was nowhere any sign of a change. This line cuts 100° at a little above 40, and 200° a little above 320.

In order to make sure that the denser form which plays so important a part in these dilatometer experiments was really metallic selenium, the material was removed from this last bulb and its specific gravity determined. The value found was 4.77.

Experiment 36 shows that metallic selenium is the only form which results from the transformation of the vitreous modification, whether at 100° or in a bath whose temperature is rapidly raised to 200°. The readings obtained at 200° are the same in each of these two cases, and are identical with that obtained by holding fused selenium at 200° until the transformation is complete.

Experiment 41. This was a further attempt to get some indication of a reverse change from the gray metallic into a less dense form, below 100°. Starting from vitreous selenium, the following readings were taken:

Temp.	Scale	Time	Temp.	Scale	Time
59°	114	11 : 15	80°	134	1 : 20
62	118	11 : 18	81	96	2 : 30
68	130	11 : 27	—	66	4 : 06
74	141	11 : 40	70	47	4 : 15
81	154	12 : 16	69.5	45	4 : 35
83	157	12 : 25	98	92	4 : 45
82	153	12 : 35	—	84	5 : 05

The experiment shows that, when the change has proceeded some distance at 81°, and the temperature is lowered to 70°, there is no sign of a recovery during twenty minutes, although the last two readings show that the transformation was not complete, i. e., that two forms were present.

Experiment 43. Confirmatory of exp. 41. This determination, which was carried on in a dilatometer filled with quinoline, yielded the following readings:

Temp.	Scale	Time	Temp.	Scale	Time
81°	112	2 : 08	70°	42	4 : 15
—	93.5	2 : 15	69.5	41	4 : 35
—	74	2 : 40	98	71	4 : 48
—	56	3 : 36	—	66	5 : 05
—	52.5	4 : 06			

Experiment 45. Carried on with the same dilatometer that was used in exp. 41. Starting from vitreous selenium these readings were made:

Temp.	Scale	Time	Temp.	Scale	Time
65°	127	12 : 32	78.5	150.5	2 : 03
71.5	139	1 : 10	80	152	2 : 16
74	143	1 : 32	81.5	152	2 : 34
77	148.5	1 : 51	78	139	3 : 07

showing that the transformation began at about 80° in this case. The temperature was then raised —

107°	178	3 : 36
125	150	3 : 38
130	122	3 : 39
156	158	

Then the dilatometer was placed in the cooler bath —

67.5°	19	3 : 51
—	17	4 : 15

The dilatometer then stood over night, and registered on the following day —

Temp.	Scale	Time
58.5°	0	

Four days later the level was again taken

63°	5	11 : 30
78	28	12 : 40

The bulb then remained at ordinary temperatures for two weeks, sometimes standing for half a day in direct sunlight. At the end of that time, a reading was again taken and gave

59°	0	
69	15	

and after standing in sunlight for a few hours more, it gave on the following day

70°	17	

Two months later a reading was again taken, and gave at

63°	4	

which shows that no change had taken place.

This experiment illustrates the complete stability of metallic selenium at ordinary temperatures and up to 60°, whether it be kept in diffused daylight or in direct sunlight.

When selenium is heated by itself to 100° it does not always go over entirely to the metallic form. Petersen (1891) found that specimens of selenium which were transformed from the vitreous into the metallic form, at whatever temperature, always contained more or less of the original material. This is illustrated by the following experiment:

Experiment 46. A quantity of vitreous selenium was heated for half an hour in a water-bath, and was then placed in a dilatometer with quinoline. The following are the readings:

Temp.	Scale	Time
74°	103	1 : 32
80	92	2 : 16
78	78	3 : 00
73	70	3 : 21
67.5	63	3 : 45

The dilatometer was, later on, heated for five hours between 45° and 60° and showed no signs of a reverse transformation, although raising the temperature afterwards to 80° showed that the transformation had not been entirely completed.

When vitreous selenium is placed in a dilatometer with water, the transformation begins at about 80° and proceeds slowly but uninterruptedly to an end, as shown by the following experiment:

Experiment 69. 3.06 grams of vitreous selenium were placed in a dilatometer provided with a capillary arm previously calibrated. The following readings were made:

Temp.	Scale	Time
64°	89	11 : 44
71	98	12 : 14
77	106	12 : 30
79	108.5	12 : 35
81	111	12 : 40

A slight transformation took place at this last temperature and the experiment was continued on the following day:

Temp.	Scale	Time	Temp.	Scale	Time
67°	86		80°	65.5	12 : 06
82	102.5		79	58.5	12 : 40
85.5	105	11 : 05	81	42.5	2 : 15
84	87	11 : 28	80	36	4 : 20
83	81	11 : 36			

and on the following day :

Temp.	Scale	Time
79°	27	11 : 20
80	26	12 : 30
—	24	3 : 30
77	21	5 : 10

The transformation may be taken as complete.

Calculating the change in density from the difference between the original and final readings at 77° and assuming the density of vitreous selenium to be 4.3, we find for the density of the metallic form by this experiment 4.77. The determination shows that no other forms make their appearance here but the two mentioned.

In another experiment, also carried on in water, a quantity of selenium was heated in a water-bath for one and one-half hours, after which no further change of volume could be noted. The mass had the familiar steel gray color. On raising the temperature to 130° no change took place. Some of it was then taken out, and placed in a dilatometer containing aniline, and heated during one and one-half hours to about 150°. This also brought about no further change, showing that in water as well as in other liquids, it is the metallic form which always results from a transformation of the vitreous modification no matter at what temperature this transformation is effected.

Conclusions from dilatometric experiments

It may seem that the experiments with the dilatometer have been needlessly multiplied. This repetition is due in part to the fact that the method of working was at first very imperfect, but mainly to the fact that the evidence to be obtained from them is both positive and negative. There is to be found in many of the textbooks a description of the gray form of selenium obtained by heating the vitreous modification to 100°, which separates this as a distinct modification from the black crystals obtained in other ways, and these experiments were begun with the expectation of finding two such distinct forms with a real transition point. It will be seen, however, that the evidence is all against the existence of any stable form except the one having a density of 4.8 and the multiplicity of the experiments only serves to render that evidence more conclusive. When selenium is heated in liquids in which it is somewhat soluble, like quinoline or aniline, or in which it is practically insoluble, as paraffin, only two modifications are obtained, the vitreous and the metallic. The metallic form is stable throughout its range, up to 220° or nearly; whereas the vitreous form goes over at any temperature above about 60° to 80° according to the liquid present. When vitreous selenium is placed in water, it behaves in the same way as it does in other liquids which do not dissolve it. Furthermore, with regard to the behavior of the element at 200°, only one form can permanently exist there. It makes no difference whether fused selenium be cooled to 200°, or whether vitreous selenium be rapidly heated to 200°, or again, whether it be allowed to go over at any lower temperature and then raised to that point — the final density at 200° is always the same and lies along the density curve for metallic selenium. Sunlight causes no change of volume in metallic selenium either at ordinary temperatures or at higher ones, up to 200°. It is not as a rule possible to raise the temperature of vitreous selenium above about 140° without a sudden change into the metallic form, but it may occasionally, by rapid heating, be brought to 180° or above before the change takes place. When metallic selenium is kept at ordinary temperatures or placed in a bath heated to 40°, 50°, or 60°, or any higher temperature, below 220°, it shows no tendency to go over into any other form.

The general character of the curves obtained by plotting the results of dilatometric determinations with selenium is illustrated by the accompanying drawing (Fig. 2).

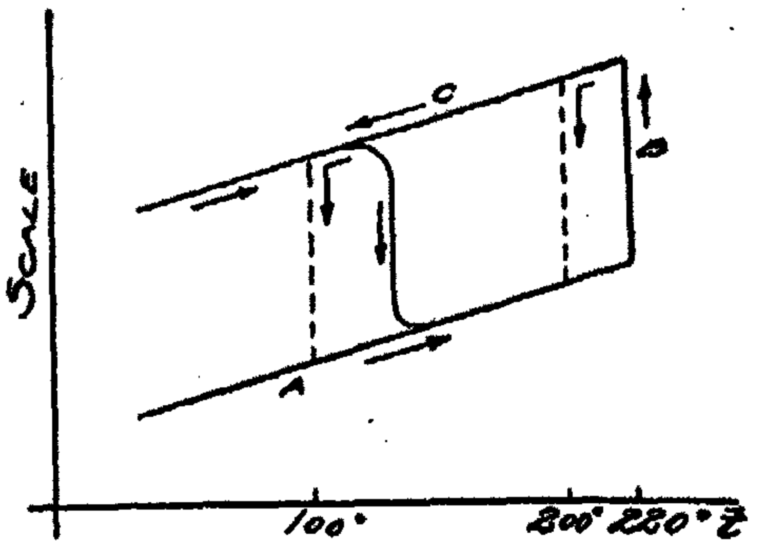

Fig. 2[1]

The line A represents the metallic form; the line B, the fusion, with formation of liquid selenium; this when cooled gives the line C; if the cooling be stopped at 200° we obtain the line C_1 leading back to A; if it be stopped at 100°, we get the line C_2 also leading back to A. Finally, if the line C be followed down to ordinary temperatures, it is not usually possible to reproduce it with rising temperature, but the change follows a curve of the general form of D, which again leads us back to the line A, for the metallic modification.

Two objections may be urged against conclusions drawn from dilatometric measurements regarding the possible transformations of a substance. In the first place, the results only apply to cases where the material studied is in contact with a liquid, in which it will always be more or less soluble; and in the second place, the results, being really only density determinations, will fail to bring out such changes as involve very slight alteration in specific gravity. This latter objection must be let stand, although the probability is always in favor of two different modifications having differences in density which lie within the range of experimental proof. To meet the first objection, a

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[1] The vertical dotted lines, beginning at the right, should be lettered C_1 and C_2. The intermediate curved line is the line D.

few density determinations were made, to fill out the gaps left in earlier investigations along this line. They will be found recorded under the corresponding heading.

Vitreous selenium is stable, by itself, at ordinary temperatures, for an indefinite time. Hittorf states that it remains for years without alteration, and the fact that the selenium of commerce is in the vitreous form, further demonstrates its permanence.

To illustrate the degree of its viscosity, a rod of it, having a diameter of about 5 mm. was fastened in a horizontal position and a weight of 200 gr. hung upon it at a distance of 6–8 cm. from the point of support. No change could be observed in it at the end of a week. On the other hand, when the substance is fused and drawn into stout threads and these are fastened horizontally, they bend almost at once by their own weight alone.

The vitreous and amorphous forms being both of them liquid selenium, but in different states of division, it follows that their solubilities must also be practically identical. Nevertheless, while the solubility of the amorphous form in carbon disulphide is always admitted, it will be found stated here and there that the vitreous form is nearly or quite insoluble in that liquid.

Thus Schützenberger,[1] after contrasting the solubility of the amorphous form with the insolubility of the metallic, adds: "Vitreous selenium is also almost insoluble in carbon disulphide." But many points in the description of selenium, in this, as well as in most of the other textbooks, are quite at variance with the truth, often, indeed, in disagreement with facts which have long been known. To show that vitreous selenium does dissolve in carbon disulphide, it is only necessary to place a piece in a little of this liquid for a few moments and follow the immediate change of color.

The data regarding the solubility in this liquid — and they apply equally for the amorphous modification — are as follows: Mitscherlich (1855) states as a result of his experiments that one

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[1] Chimie générale, 1, 438.

hundred parts of carbon disulphide at 46.6° dissolve 0.1 part of amorphous selenium, and at 0°, 0.016 part. Rammelsberg (1874) says that one part of selenium (probably amorphous) is soluble in 1376–2464–3746 parts of carbon disulphide at 20°. We have no details of either of these determinations, but Mitscherlich had noted for the vitreous form as well as the amorphous, that on standing in contact with carbon disulphide, red crystals appear, and he had interpreted this in the case of the vitreous form as not being a change in the mass of the material, but a superficial alteration involving successive solution and recrystallization.

To determine the correctness of this explanation I placed some pieces of vitreous selenium in carbon disulphide, and left them in diffused daylight. On the following day the surfaces were found to have lost their black vitreous lustre, and to have acquired a dull brownish iridescence; they were, moreover, everywhere covered with minute but well-formed, glittering, transparent red crystals, some of which were loose in the bottom of the vessel, but most of them adhering to the mass of the selenium. After twelve days more, there was no further visible change. The fragments were then removed from the solution, and when broken were found to have their original black fracture within. This shows that Mitscherlich's explanation is correct. The change does not extend within, but stops as soon as the entire surface has become coated with crystals or a crystalline film. It shows also that in all likelihood the crystals are much less soluble than the original material; otherwise this change would be difficult to explain. My experiments have further shown that the change goes on much more rapidly than Mitscherlich supposed.

Now the observation just recorded goes far to clear up the discordant solubility results of Rammelsberg. It is probable that they were obtained by successive determinations from the same material, and that their variation corresponds to the change going on in the solution as it passed from a state of saturation with respect to amorphous selenium, to a state of saturation with respect to the red crystals themselves. Hence, while his first value, according, as it does, fairly well with Mitscherlich's, probably represents the solubility of amorphous selenium, the second represents nothing definite at all, and the third is possibly somewhere near the value for the red crystals.

A further experiment of mine showed that vitreous selenium in carbon disulphide in the dark, remained unchanged for six days. At the end of that time, it was allowed to stand in the light for a day and was then found covered with crystals.

Vitreous and amorphous selenium are known to be soluble in various other liquids, but few quantitative measurements have been made.

Retgers (1893), using the powder of commercial vitreous selenium, found its solubility in methylene iodide at 12°, to be 1.3 parts in 100; from this solution, on evaporation, the selenium separates in monoclinic, blood-red leaflets, and also in black opaque aggregations, the latter probably metallic selenium. Schneider (1866) found that when amorphous selenium is allowed to stand in contact with selenious bromide for eight days, with occasional heating to 70°–80°, a solution is obtained which contains in 2 gr. of the solvent — probably at ordinary temperatures — 0.44 gr. selenium.

Rathke (1869), in endeavoring to find a liquid which would yield good crystals of the metallic form, noted the solubility of vitreous selenium in carbon di-selenide, selenium di-ethyl, sulphur di-ethyl, and in selenious chloride, which last is capable of taking up very considerable quantities of the element. All forms of selenium dissolve in sulphuric acid, forming a green solution, but no exact study has been made of the degree of solubility. Some further notes on solubility will be found later on, in the description of the other modifications.

Petersen (1891) found it impossible to get vitreous selenium quite pure. He found that samples prepared by rapid cooling of the fused mass were never free from material which was insoluble in carbon disulphide, though his difficulty may possibly have arisen from impurities in the material.

Regnault, in studying the rate of cooling of melted selenium to find whether there were any irregularities in the change of temperature, made a series of observations between 260° and 40° and found no signs of any irregularity. The apparatus consisted merely of a vessel filled with a large quantity of selenium, with a thermometer standing in the mass. In order to confirm this result, he placed the apparatus in an air-bath at 100°. The readings, which were taken every minute, are as follows:

241.6°	175.95°	148.1°	137.85°
229.8	170.9	146.3	137.0
219.3	166.4	144.7	136.25
210.2	162.4	143.25	135.5
201.7	158.8	142.0	134.7
194.4	155.6	140.75	133.9
187.6	152.9	139.65	133.2
181.6	150.4	138.75	

From here on, the readings were made every five minutes:

133.2°	115.0°	114.05°	116.0°
129.2	113.4	115.9	113.35
125.35	112.8	117.9	111.25
121.9	112.6	120.75	109.65
119.1	112.55	121.3	108.45
116.8	113.0	118.9	107.55
			106.8

It will be seen that at about 113° there is a marked rise of temperature, followed by a uniform drop like that which preceded. What the cause of this may have been, it is impossible to say; perhaps a partial transformation into metallic selenium, although at that temperature the transformation should have been complete if it had taken place at all; possibly a transformation into one of the red crystalline forms; or possibly merely an experimental variation. At any rate, the observation being of an exceptional character, is worth recording.

Electrification of the vitreous form

Seebeck (1826) reports that a rod of selenium (no doubt the vitreous form) becomes negatively electrified when rubbed, though less strongly than sulphur.

Riess (1845) confirmed this observation of Seebeck. Berzelius had been unable to observe this phenomenon, though he records in his Lehrbuch that it was noted by Bonsdorff.

My experiments showed that vitreous selenium, when freshly prepared by pouring the melted material on a cold stone slab, shows very marked electrification.

Refraction and dispersion of vitreous selenium

These properties were investigated by Sirks (1871) who found the following values:

n_A	n_a	n_B	n_C	n_c	n_D
2.653	2.691	2.730	2.786	2.857	2.98

Thus the element shows strong dispersive power, as well as very high refraction.

Diathermancy

Schultz-Sellack (1869) furnishes the following data for the diathermancy of vitreous selenium:

Thickness of the selenium plate	Percentage of heat passed through	
	from lamp black at 100°	from an illuminating gas flame
0.4 mm	50	36
3.0 "	16	5

2. Soluble selenium

It is familiar to everyone who has carried out the reduction of selenious acid by sulphurous acid, in solution, that when the two liquids are mixed, there is often no precipitation at first; the color changes from yellow to a more or less deep red, and only after the lapse of a certain time is a deposit of red selenium formed. This makes its appearance then as a red powder, or as a golden or red translucent skin upon the sides of the vessel.

Schulze (1885) has carried out experiments upon these colored solutions, and his observations, as far as the solubility of the element is concerned, have been confirmed by Muthmann (1887). Schulze's results point to the existence here of a mono- and perhaps a di-selenium tri-thionic acid, $H_2S_2SeO_6$ and $H_2SSe_2O_6$. These acids are instable in the presence of mineral acids, and it is perhaps by this breaking down that the red solutions are formed which afterwards deposit amorphous selenium.

Schulze has observed that the red selenium precipitated from such solutions redissolves if an excess of water be added, and that it loses this solubility in a short time, especially if exposed to the light. The solution is stable in the dark, but when allowed to stand in the light, deposits selenium in the form of a red film or skin. By dialysis all foreign substances can be removed. The solution may be boiled without decomposition, but the addition of salts and acids throws out the selenium. Selenium in this form has very strong coloring power; solutions of 1 part in 10,000 parts of water are distinctly reddish.

If we assume that this freshly precipitated selenium forms solutions in the ordinary sense of the word, and loses its solubility on standing, we are led to the conclusion that we have here to do with a distinct form of the element. If on the other hand we suppose, — what is highly probable, — that the acids described by Schulze are colorless, and that the solutions owe their color to selenium in suspension, then it is quite conceivable that the change in the substance on standing is simply one of aggregation, the extremely small particles deposited from suspension clotting together to larger masses incapable of re-solution. This accords very well with the nature of the red powder and with the familiar observation that at 40°–50° it clots together to a soft sticky mass.

3. Amorphous selenium

Even when freshly precipitated selenium is merely suspended in the liquor, it often remains for hours without settling down. If the vessel be laid aside and the precipitate allowed to come down slowly it forms a soft mass in the bottom of the vessel, resembling in texture and mobility a soft coagulated jelly. When shaken, it does not at first go into powder, but breaks along irregular lines. When dried, it forms an impalpable powder which cannot easily be completely removed from any material with which it has come into contact, — the hands, filter-paper, etc.

Hittorf (1851) records that the red powder of selenium when subject to the heat of the sun's rays becomes partially crystalline, but this was probably a heating effect, or he may have been deceived by the change of color. I have repeated the experiment and find that there is a rapid change in color, but the product appears to be still the amorphous form, though much darkened and clotted together.

When gradually warmed, the powder begins to be somewhat adhesive and clots together, and at about 50° forms a soft mass, at the same time darkening in color; when this mass is cooled down, it is found to have the brittleness and, if it has been pressed together, the fracture of the vitreous form. This clotting together on warming is a character of the powders of viscous liquids, as is illustrated by the following experiment: Some sealing-wax was reduced to as fine a powder as possible in a mortar, then placed in water and warmed. The powder became first of all adhesive, and at 40°–50° began to clot together. On further raising the temperature, it became quite soft, and after cooling down, it assumed the ordinary brittleness of sealing-wax. The behavior of amorphous selenium is so exactly similar that it would scarcely have been possible to tell which of the two substances was in hand, but for the difference in color. By placing some of the powder in a pastille press, and striking a few sharp blows upon it with a hammer, a hard black mass is obtained, which has a conchoidal fracture, though less brilliant than that of vitreous selenium prepared in the ordinary way. The red powder is never quite free from dust, which interferes with the experiment. These properties all go to show the identity of the amorphous and vitreous forms. If there be any difference at all between them it is a very slight one, and would not justify their being considered as two distinct modifications. For a discussion of the possibility of such a difference, see the section on specific gravities. Hittorf (1848), Regnault (1851), and others have remarked upon their identity. The amorphous form of selenium is the one which separates by preference in all cases where selenium is rapidly set free, either by decomposing one of its compounds or by precipitation from solution or vapor. This is in accordance with the rule laid down by Ostwald.[1] The amorphous form is obtained in any of the following ways:

(1) In the ordinary method of purification by dissolving in potassium cyanide and then reprecipitating with hydrochloric acid.

(2) When selenious acid is reduced by sulphur dioxide. Even if both solutions be previously heated, it is still the amorphous form which comes out. In order to test this further, a boiling solution of selenious acid was added to a boiling solution of potassium sulphite; now at 100° vitreous or amorphous selenium goes over rapidly into the metallic modification; nevertheless, on mixing the above solutions, the selenium makes its appearance first as a red precipitate, and only after the lapse of a certain time does this become black. In place of sulphur dioxide we may use, in this reaction, iron, zinc, hydrogen, phosphorous acid, stannous chloride, ferrous chloride, chromous chloride, etc. Klages (1898) records that there is an emission of light when selenious acid is reduced by hydrogen.

(3) From solutions of selenium in concentrated sulphuric acid, on the addition of water.

(4) By the decomposition of selenious bromide by alcohol (Schneider, 1866).

(5) By sublimation of the element itself, whereby the amorphous form condenses in the cooler parts of the tube, though it is possible also to obtain crystals of the gray form in this way (Bornträger, 1881).

(6) From various compounds of selenium when decomposed, such as the alkaline selenides (Uelsmann, 1860).

(7) By the electrolysis of solutions of selenious acid, or by passing a current through a selenium cell, whereby amorphous selenium makes its appearance at the anode (Bidwell).

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[1] Zeit. phys. Chem. 22, 294 (1897).

When melted selenium is rapidly cooled, the vitreous form is always obtained. This case is not like the above, being merely an instance of supercooling.

Amorphous and vitreous selenium show an increased reactivity compared with the other forms. This is of importance in the purification of the element by the cyanide method because if selenium be heated in a solution of potassium cyanide, it goes over to the metallic form, and long boiling is then required to bring it into solution, whereas if the amorphous or powdered vitreous material be placed in a cold cyanide solution, the reaction is complete in a very short time. This fact was observed by Schjellerup,[1] but has been lost sight of in most of the more recent work. Its bearing upon analytical methods and upon commercial processes might prove important.

Behavior of amorphous selenium in solvents

Mitscherlich (1855) observed that when amorphous selenium is allowed to stand in carbon disulphide for some weeks, it becomes darker in color and more compact, and changes to a mass of red crystals which are, like the original substance, completely soluble in carbon disulphide, though not readily so. The observation was repeated by Schneider (1866) and later by others. Wishing to repeat the experiment and to find whether the change is influenced by light, I proceeded as follows:

Experiment 44. A small quantity of amorphous selenium was placed in carbon disulphide, the tube sealed and allowed to stand in diffused light. After one day the selenium had become very dark in color, and showed bright crystal faces. On stirring the tube, it was found that this change was only superficial; but upon exposing fresh surfaces, these darkened very rapidly, and in two days the mass had become entirely crystalline in appearance and had assumed a uniform deep cherry red color. The volume of the selenium had also materially diminished. This leads to the conclusion that the change into the crystalline modification goes on much faster than had been supposed, and also

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[1] Ann. 109, 125 (1859).

that it is in some way affected by light. How far the light effect goes will be better understood from the following experiment:

Experiment 50. Amorphous selenium in a tube of carbon disulphide, in the dark. After seven days the mass of selenium had become almost entirely crystalline, but showed no change of color. After standing for twelve days longer, the color was a dark cherry red, much deeper than the original color, and the entire mass had become crystalline. This change of color between the two periods may have been due to the exposure of the tube on the first examination, or it may be that the crystals ultimately assume the deeper color even in the dark. Detailed experiments to trace out the connection between these color changes were not undertaken, but it is clear that the absence of light, though it retards the darkening of color, does not prevent the formation of crystals. A later experiment in direct sunlight showed a complete change in one day, the mass becoming uniformly dark in color and completely crystalline.

After these experiments, I turned to the consideration of the behavior of amorphous selenium in contact with other liquids.

Experiment 53. In water. After four days, there was no visible change; after eight days, a perceptible darkening; after fourteen days, this change of color had become more distinct, but no crystal faces could be observed. During this period of time, the tube had stood at least three afternoons in direct sunlight. After one hundred days, the color was much darkened, but still red.

Experiment 52. In absolute alcohol. After four days the powder had become noticeably darker in color and this change progressed steadily to the end. After eleven days crystal faces made their appearance, and after fifty days the mass was everywhere crystalline and almost completely black.

Experiment 51. In benzene. After three days there was a visible change of color. After four days glittering crystal faces became noticeable, and after six days the mass had assumed a uniform deep maroon or cherry red color, and was everywhere crystalline. During ten days more, there was no change in appearance and the experiment was then stopped. Experiments 51 and 52 were made under the same conditions as 53 with regard to sunlight.

Experiment 56. In quinoline. The material becomes black at once, in diffused daylight. Under the microscope the progress of the change may easily be watched. It spreads gradually through the mass under ordinary illumination, and is almost instantaneous in direct sunlight. There is no perceptible shrinking together of the selenium, hence the change is probably not the same as that which is brought about in amorphous selenium by raising the temperature. It remains here in a state of extremely fine division and when shaken with the quinoline, does not settle again to the bottom for hours. After the first half hour no further change in color could be observed, although the period of observation extended over forty days. It was impossible to find any signs of crystallinity either with the eye or under the microscope. At the close of the experiment, the selenium was removed from the tube, washed with benzene, and dried. It showed no sign of melting at 215°, but at 225° melted at once. When shaken in carbon disulphide, it remained for a long time suspended in the liquid — much longer than ordinary amorphous selenium — but, on filtering, the solvent came through clear and colorless.

This shows beyond a doubt that the material goes over in quinoline to the metallic form, and not to the crystalline modification which is obtained, as we have seen, in other liquids. There is here not merely a difference in the rate of change, but a difference in its nature, brought about by the presence of the liquid. It was important then to learn a little more of this change.

A larger quantity of amorphous selenium was placed in quinoline, in diffused light. It remained unchanged for a few moments, then began to darken rapidly, and in fifteen minutes was completely black. After thirty minutes benzene was added and the material filtered and dried. It did not melt at 200°.

The specific gravity was found to be 4.65. A second determination after further washing and drying gave 4.59. The variation is somewhat large, but it must be remembered that only a small quantity of material was used. The results show, at least, that the change to the metallic form was not yet complete. A larger quantity—about 1 gram—of amorphous selenium was then placed in quinoline and left for two days. At the end of that time a specific gravity determination yielded the result 4.86. Hence the change which is at first so rapid, is only superficial. It is probable that each little particle of the amorphous form becomes covered with a coating of the metallic modification which then protects it from further immediate change.

The question arises, whether the action of quinoline is catalytic, or whether it is an effect of solubility, or in some other way proportional to the amount of that liquid present. To answer this, five experiments were made in liquids composed of benzene and quinoline in the following proportions:

(1) Pure benzene
(2) 2 cc " + 0.1 cc quinoline
(3) 2 cc " + 0.2 cc "
(4) 2 cc " + 0.5 cc "
(5) 2 cc " + 2.0 cc "

The selenium in No. 5 blackened within a couple of minutes. That in No. 4 was perceptibly slower in changing, but reached the same end state. In No. 3 it was still not entirely blackened after twenty minutes, and that in No. 2 was, after twenty minutes, only very slightly darker than that in No. 1, which had shown no change at all. On the following day, all except No. 1 were completely black. In (4) and (5) the substance remained, after shaking, a long time in suspension. In the others this was much less marked. It appears from these experiments that the velocity of the change is roughly proportional to the concentration of the quinoline.

An experiment to find whether the reaction goes on in the absence of light showed that it did so, although the results were not accurate enough to show whether the velocity suffers a diminution in the dark.

A number of experiments were then tried with amorphous selenium in various liquids, the results of which are given below:

Aniline. — After one-half hour, perceptibly darkened; after two days, completely black.

Thiophene. — After one-half hour, no change; after three hours, crystalline without change of color. On the following day, the material showing no further change, 0.5 cc quinoline was added. After fifteen minutes, the selenium had become black, but there were still glittering crystal faces to be seen. After half an hour, these had all disappeared and the mass was uniformly black. This experiment demonstrates the power of quinoline to bring about the same change in the red crystals that it causes in amorphous selenium itself.

Pyridine. — After ten minutes, no change; after one hour, completely black.

Toluene. — After five hours, crystalline and darker in color. No further change after seven days. After thirty days, darker in color.

Benzonitrile. — After one day, crystalline, and darkened. After thirty days more, no further change.

Benzyl cyanide. — After one day, completely black. After fifty days, no further change.

Benzimido-butyl-ester. — After one hour, black; after fifty days, no further change.

Propyl aldehyde. — After two days, no change; after three days somewhat darker, but no crystals. After thirty days, very dark and crystalline.

Piperidine. — Black at once.

Amyl nitrite. — After three days, unchanged. After thirty days, partially crystalline; color unchanged.

Ethyl acetate. — After one day, unchanged; after two days, somewhat darkened; after three days, almost black, without crystal faces; after thirty days, completely crystalline.

Isobutyric acid. — After three days, unchanged; after thirty days, slightly crystalline, no change of color.

Aqueous ammonia. — After one hour, completely black. After fifty days, the same.

Acetophenone. — After one day, much darkened, and crystalline. After three days, almost black, completely crystalline; after thirty days, no further change.

Nitrotoluene. — After one day, crystalline and darkened. No further change after thirty days.

Brom-nitro-benzene (*m*) *in benzene.* — After three hours, crystalline. No further change after thirty days.

p-β-anisaldoxime in alcohol. —After one day, much darkened; after two days, completely black, without crystals. After fifty days, the same.

Hydroxylamine hydrochloride in water. — After three days, unchanged; after thirty days, somewhat darkened in color, not crystalline. Potassium hydroxide was then added, to liberate the base; this brought about no further change in the selenium.

Di-nitro-benzene (*m*). — After three hours, unchanged. After one day, partially crystalline. After two days, completely so. The change to the crystalline form is always accompanied by a darkening in color, unless otherwise mentioned.

Di-methyl-aniline. — After one-half hour, unchanged; after three hours, crystalline; after thirty days, no further change.

Nitroso-β-naphthol. — After one-half hour, unchanged; after three hours, crystalline; after three days, no further change.

Urea in alcohol. —After two days, very slightly darkened; after thirty days, darkened in color, not crystalline.

Acetone. — After three hours, darkened; after two days, black, no crystals; after thirty days, black, completely crystalline.

Ammonium sulphocyanate in water. — After thirty days, unchanged.

Picric acid in alcohol. — After thirty days, unchanged.

Tri-ethyl-amine. — Begins to blacken at once; after one day, completely black; after fifty days, the same.

Phenyl hydrazine. — Begins to blacken after a few minutes; after one day, completely black; after fifty days, black, minutely crystalline.

Benzyl-amine. — After one day, darkened; after fifty days, crystalline, almost black.

Propylene bromide. — After one day, completely crystalline, red; after thirty days, much darker in color.

Di-phenyl-methane. — After one day, unchanged; after fifty days, deep red, crystalline.

Ethyl iodide. — After one day, completely crystalline, red.

Hexamethylene-amine in alcohol. — After one day, nearly black, not crystalline; after fifty days, black.

Acet-anilide in alcohol. — After one day, very slight darkening; after fifty days, considerably darkened; about the same as in alcohol.

Potassium hydroxide in water. — After one day, unchanged. After thirty days, considerably darkened, not crystalline.

Ammonium chloride in water.—After thirty days, unchanged.

Potassium ferrocyanide in water. — After thirty days, unchanged.

Mono-methyl-aniline. — After one day, unchanged; after thirty days, entirely crystalline.

Chloroform. — After one day, unchanged; after thirty days, entirely crystalline.

We see from these results that the substances studied may be divided broadly into three classes.

(1) Those which have little or no action on amorphous selenium.

(2) Those which transform it into the crystalline red modification.

(3) Those which transform it into the metallic modification.

In the first class we find water, hydroxylamine hydrochloride, hydroxylamine, urea, ammonium sulphocyanate, picric acid, acet-anilide, potassium hydroxide, ammonium chloride, potassium ferrocyanide.

In the second, alcohol, benzene, thiophene, toluene, benzonitrile, propyl aldehyde, amyl nitrite, ethyl acetate, isobutyric acid, acetophenone, nitrotoluene, brom-nitro-benzene, di-nitro-benzene (*m*), di-methyl-aniline, nitroso-β-naphthol, acetone, propylene bromide, ethyl iodide, mono-methyl aniline, chloroform, phenyl hydrazine, benzyl-amine, di-phenyl-methane.

And in the third, quinoline, aniline, pyridine, benzyl cyanide, benzimido-butyl-ester, piperidine, tri-ethyl-amine, hexamethylene-amine, *p*-β-anisaldoxime.

The substances which are most active in bringing about the change to the metallic form will be seen to be ring compounds containing nitrogen in the ring; these without exception all show the same behavior. All the substances which cause this change are nitrogen compounds, but not by any means all nitrogen compounds are capable of causing the change; thus, while aniline acts rapidly in transforming amorphous selenium into metallic, both mono- and di-methyl-aniline change it into the red crystalline form. It is probable that further study in this field would bring out very interesting results. Meanwhile, it looks as if it could not be a question of solubility alone which explains the difference of behavior of these various liquids.

To determine whether amorphous red selenium would distil over in carbon disulphide to the black form, at ordinary temperatures, an experiment was made in a Λ-shaped tube filled with carbon disulphide, some of the amorphous substance being placed at one end and some of the black crystals separated from sulphuric acid in the other; but, although the tube remained for several weeks, no change in the size of the black crystals could be observed. The amorphous material changed in a short time to the crystalline variety, but even this, in virtue of its higher solubility, should have displayed the phenomenon; probably the time allowed was too short.

4. Red crystalline selenium

The methods by which this form may be obtained have been sufficiently illustrated in the description of the behavior of the amorphous form in solvents. The direct change from the vitreous or amorphous modification to the red crystalline in the absence of solvents, has, as I have stated elsewhere, never been observed with certainty. There is no obvious reason why this change should not go on, and it is quite possible it could actually be observed by bringing the two forms in contact at a moderate heat.

As an exception to the general rule that selenium separates in the amorphous state when set free, it may be noted here that solutions of selenium in carbon disulphide throw down, on the addition of benzene, a shower of minute glittering plates, of pale red color; the separation is not instantaneous.

The behavior of vitreous selenium in carbon disulphide and Rammelsberg's determinations of the solubility of the amorphous form, point to the conclusion that the red crystalline form has, as we would expect, a lower solubility than those others. Exact measurements in this field are still wanting. The crystals which are obtained from carbon disulphide are very beautiful in form and color, though small. They are readily broken under pressure, and yield a red powder which is indistinguishable from the amorphous modification. The red crystals, which have, in the mass, a dark maroon color, are quite stable at ordinary temperatures. Mitscherlich, who first obtained and studied them, states that they are stable at 100°, but go over at 150° to the metallic form. Rammelsberg records later that they are instable even at 100°, but Muthmann (1891), who separated two distinct crystalline forms, places the limit of stability for the first, the ordinary form, at 110°–120°, and for the second at 125°–130°. The second form is, according to Muthmann, stable at 110°.

No further work has been done upon these two forms, the crystallographic properties of which will be considered below.

If their relationship to liquid selenium on the one hand, and to the metallic form on the other, is what I have supposed it to be, then the red crystals should have an instable melting-point below 217°. Mitscherlich records an observation bearing upon this, to the effect that these red crystals melt if rapidly heated to 200°.

This observation is perfectly easy to repeat, but it does not prove that the crystals have a melting-point at that temperature. We know, from Regnault's observations, that the heat of reaction in passing from the amorphous to the metallic form is large enough to raise the temperature of the selenium about 200°; but since the red crystalline form is intermediate between these two, it is quite probable that a considerable quantity of heat is evolved when it is carried over to the metallic form; hence this apparently real melting-point may represent only what we may call a case of self-fusion, in which a part of the material in going over to the metallic form raises the temperature of the remainder to its melting-point. When some of the powder of the crystals is dropped on a platinum plate, heated by means of an oil-bath to 170° or above, the powder melts, and this fusion is followed by an immediate transformation to the metallic form. Below 170° the change goes on more slowly and without fusion. By dropping the powder into a test-tube plunged in the bath, substantially the same results are obtained. Since the crystals are not themselves a form of the liquid modification, it is only necessary to show that, in melting, their temperature does not rise to 217° in order to establish the instable melting-point. For this purpose, the powder of the crystals was mixed with some high-melting organic compounds, kindly supplied to me by Dr. C. E. Brewer in this laboratory. The compounds used are: anisic acid, melting-point 180°; tri-methyl-acetyl-gallein, 196°; and gallein acetate, 215°. The corresponding bath temperatures used were 170°, 190°, 205°, respectively, and in no case was there evidence of fusion of the organic substance. The best results were obtained at 205°, the fusion of the selenium itself being less complete at the other temperatures; at this point the selenium was completely fused, whereas the crystals of the gallein acetate, although in intimate contact with the selenium, remained unchanged.

This experiment, taken in conjunction with the preceding one, shows that the red crystalline form has probably an instable melting-point at 170°–180°.

The crystallography of this form of selenium was first studied by Mitscherlich (1855). He noted that selenium separates from carbon disulphide in two different crystal habits: (1) as thin, transparent, red, brilliant leaflets, and (2) as grains which are so intensely colored as to appear opaque and almost black, although thin fragments of them show the transparency and color of the leaflets. He obtained the largest crystals by placing amorphous selenium together with carbon disulphide in a sealed tube, and subjecting this to successive changes of temperature between that of the room and a point somewhat below 100°. The crystals so obtained were scarcely 1 mm broad, but had such well developed faces that it was possible to determine the angles by means of the goniometer.

Mitscherlich finds that the crystals are monoclinic; the better developed ones show a great variety of faces. He made a good many measurements of the angles for which, however, the original article must be consulted.

Muthmann (1891) was able to separate two monoclinic forms, both obtained from carbon disulphide solutions; and he found that they possessed different degrees of stability. With regard to the form studied by Mitscherlich, Muthmann's results are confirmatory in the main. The axial relationships, he found to be

$$a : b : c = 1.63495 : 1 : 1.6095$$
$$\beta = 75^\circ 58'$$

The commonest faces are OP, $\infty P \infty$, $+P$ $-P$, and $\infty P2$, though Muthmann also finds many other faces upon the better developed crystals. The color is orange red with a not very pronounced semi-metallic lustre.

The second form appears as short thick prisms with very pronounced semi-metallic lustre; they also are monoclinic, but the axial relationships are different:

$$a : b : c = 1.5916 : 1 : 1.1352$$
$$\beta = 86^\circ\ 56'$$

The observed faces were ∞P, OP, $\infty P \infty$, and $P\infty$. This form comes out sometimes as leaflets which are then easily confused with crystals of the first form. The color is deep red.

5. Metallic selenium

Some of the methods by which this modification can be obtained from the others, have been already indicated. It is in the mass a steel gray metallic substance; when powdered, it gives a black powder, but if the grinding be made finer still, the sub stance is seen to be red. Thus, if a little of the powder be rubbed upon a soft porcelain plate, it becomes so red that it cannot be distinguished from the other forms in the same state of division. There are in the literature many conflicting statements regarding the powder and streak of this modification. Thus, Rathke (1869) states that it is black even in the finest powder; and the streak is almost always given as black. Mitscherlich, on the other hand, observed that the streak was red. In my experiments on the changes of the amorphous form in liquids, I observed that the powder which results in quinoline and some of the other compounds used, while it appears black to the eye, always shows a purplish color under the microscope; and it is easy to rub this into a red powder in the way indicated.

In view of the possibility of a reverse transformation from the metallic form back to the vitreous at lower temperatures, I made some experiments upon the red powder obtained from metallic selenium in order to show that it really retained the properties of that form. The first of such experiments was made with some of the powder out of quinoline, and was far from reassuring. I found that when this is rubbed up very fine, so that it is quite red, and then treated with carbon disulphide, it gives a colored solution, indicating the presence of one of the soluble forms of selenium. The powder obtained from some gray metallic selenium which had been prepared by heating the vitreous form for some time to 150° gave the same result, although in this case the resulting color was less intense. When selenium is dissolved in hot sulphuric acid to purify it, there is often a separation of crystals about the upper surface of the liquid. They are in the form of gray metallic scales and as they separate at a high temperature, it was to be assumed that they would be quite free from the amorphous modification. When finely powdered, they also give a red powder, and this when brought into cortact with carbon disulphide colors it, though only very slightly. Plainly, then, the purer the metallic modification is, the less soluble is its powder, in carbon disulphide; and I presume therefore, that if one could prepare the metallic modification in quite pure condition, it would no longer show this property at all. With regard to the presence of soluble selenium in the metallic form which was prepared from the vitreous substance, Petersen (1891) has observed the same thing. He found that the purest metallic selenium he could prepare always contained about one percent of a form soluble in carbon disulphide.

The quantity of material used in the above tests was small, but it has been mentioned in speaking of soluble selenium that one part of that material in 10,000 parts of water, imparted a distinct color to the solution; hence the quantity of the soluble form which would be required to color one or two cc of carbon disulphide, would without doubt, be extremely small.

In making some experiments upon the effect of heat on these red powders, I found it impossible to prepare one which did not turn gray on heating to about 200° in an air-bath; but on rubbing up again, even at that temperature, the red color always reappears. This observation I am somewhat at a loss to explain. It is due, perhaps, to an alteration in the state of aggregation, but how this is brought about with a substance which melts sharply at 217° without previous softening, and in a powder which is a mixture of selenium and foreign matter, it would be difficult to say.

In addition to the method of preparation by direct transformation of the other forms, metallic selenium may be obtained by the spontaneous decomposition of solutions of the alkali selenides in contact with the air; it then forms a crust consisting of very small crystals, which were considered by Berzelius to be tetragonal.

Fabre (1887) mentions that selenium separates in the metallic form when hydrogen selenide is decomposed by moist oxygen. It is soluble in many organic liquids at high temperatures; in the dilatometer experiments recorded above, beautiful, leaf-like crystals were obtained on heating to 230° with quinoline, and cooling down. Ethyl benzoate, aniline, naphthalene, and other organic substances also dissolve it at high temperatures.

Fröbel (1840) made a microscopic study of the crystals which separate from a solution of ammonium selenide and pronounced them to be orthorhombic.

The crystal form of metallic selenium has been studied by Muthmann (1890) who prepared the crystals by sublimation. Earlier observers had in most cases studied those crystals which separate from solutions of selenides of the alkalies, and in this way none were obtained of sufficient size to make measurements possible. Muthmann finds them hexagonal, rhombohedral and fully isomorphous with tellurium. The observed faces were ∞R and R.

6. Heat conductivity

Bellati and Lussana (1887) observed that the heat conductivity of selenium was increased by illumination. They covered a circular plate of crystalline selenium with the double salt HgI_2CuI_2, and heated it at a point by means of a hot platinum wire. The double iodide is red at ordinary temperatures, brown above 70°, and hence the area of change of color is a measure of the heat conductivity. They guarded against heating effects from the source of light and found that direct sunlight increased the heat conductivity 8–25 pct. Even the light of a gas flame had a perceptible effect.

7. Heat of transformation of liquid selenium into the metallic modification

The first determination of this heat value was made by Regnault (1856). The figures obtained by him have scarcely more than a qualitative value, but are quoted here for the sake of comparison with the later results of Petersen (1891).

Regnault's method was to place a mass of about 200 grams of vitreous selenium in an oven at 100°. A thermometer standing in the selenium was then read every minute. When the temperature reached about 98° the substance began to go over to the metallic form and the temperature rose to about 214°, subsequently dropping to 100°. The main corrections are (1) for the heat absorbed in the containing vessel and (2) for the loss by radiation; the first of these is made on the basis of a previous determination of the water-equivalent of the vessel, the second by noting the normal rate of change per minute in the temperature of the selenium when no transformation was going on in the mass. Regnault reached the conclusion that the reaction set free enough heat to raise the temperature of the selenium from 98° to about 329°, i. e. through 231 degrees. A second determination was made by another method which is even less exact, and the results so obtained indicated that the heat of reaction would raise the mass of selenium from 0° to 180°.

Regnault concludes that vitreous selenium in passing over to the metallic form sets free enough heat to raise its own temperature about two hundred degrees. In other words, taking the specific heat of vitreous selenium as 0.1, we have the value about 15 K for one gram-equivalent of selenium.

Before passing on to consider the determinations of Petersen we must mention the researches of J. Thomsen[1] which bear indirectly upon this point and are of especial interest in connection with a possible difference between the vitreous and amorphous forms of selenium. Thomsen determined firstly the heat involved in the reaction:

$$SeO_2Aq + 2HClAq + 2NaSHAq = 2NaClAq + 2H_2O + Se + S_2.$$

The solutions used had the molecular composition:

$$\begin{aligned} &A \ldots NaSH + 616.7\, H_2O \\ &B \ldots SeO_2 + 2HCl + 1500\, H_2O. \end{aligned}$$

In each experiment 1/30 of the corresponding weight of A and 1/60 of that of B was used.

The total heat value is made up as follows:

$$R = \begin{cases} 2(NaOHAq,\ HClAq) - 2(NaOHAq,\ SH_2) \\ + 2(H_2,\ O) - 2(H_2, S) - (Se,\ O_2,\ Aq) \end{cases}$$

R is found experimentally to be 733.98 K; introducing this along with previously known values, we get

$$733.98 = 274.80 - 249.80 + 1367.14 - 94.80 - (Se,\ O_2, Aq),$$

whence $(Se, O_2, Aq) = 563.36$. It will be seen from the nature

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[1] Thermochem. Unters. 2, 269, 313.

of this reaction that the heat value here found refers to amorphous selenium.

Thomsen determined, secondly, the heat of formation of the chloride Se_2Cl_2 from "ordinary amorphous selenium, prepared by cooling the melted substance", i. e. from the vitreous form.

Three separate determinations gave 221.29 — 219.85 — 223.35, the mean being 221.5. From the chloride Se_2Cl_2 he determined the heat of formation of the chloride $SeCl_4$, and finally by finding the heat of reaction of this substance with water, obtained as an independent result for the reaction (Se, O_2, Aq), 559.86. Thomsen considers these two results in satisfactory agreement, although he suggests that a slight difference in the physical state of the selenium in the two cases may explain the variation. It is of interest to note that the difference is in the direction of greater heat of reaction for selenium in the amorphous state. This falls into line with what is said below in the chapter on specific gravities, regarding a possible difference between the two forms.

Fabre (1887) measured the heat of transformation of liquid selenium into crystalline, by placing the material in the calorimeter and warming it by adding sulphuric acid to water in a larger tube, which surrounded the one containing the selenium; after the reaction was over, these tubes were broken and a correction then introduced for the heat of dilution of the sulphuric acid in the total water-content of the calorimeter.

By this ingenious device, he was able to measure directly the heat of reaction. His results are as follows:

For one gram-equivalent of vitreous selenium

52.2 57.2 58.2 mean 55.8 K.

For red precipitated selenium

55.8 51.2 mean 53.4.

These results are practically identical, within the limit of experimental error. They indicate that Regnault's value is far too low, a conclusion that is only confirmed by later results. The material used by Fabre was afterwards tested as to its specific gravity, and found to give as a result, 4.78 for the first, and 4.79 for the second; hence the transformation was probably complete.

Fabre used an indirect method to confirm these conclusions, namely the action of bromine in bromine water, upon selenium. For the metallic modification he found the values 431.6 — 432.4 — 421.0; mean 429. Unfortunately, we are not told how the material was prepared.

The crystals which separate from solutions of selenides of the alkalies gave 432 — 434; mean 433. Vitreous selenium prepared by rapid cooling, on a porcelain plate, from the fused state, gave 480 — 495.6 — 485.2; mean 486.8. The difference in the two cases may be taken at about 57 K, a result which agrees fairly well with that obtained by direct measurement.

Finally Petersen (1891) redetermined by indirect methods the heat of transformation from the amorphous to the metallic and to the red crystalline form.

For the heat of formation of the chloride Se_2Cl_2 from vitreous selenium prepared by pouring the melted element into water, he obtained values which vary in four experiments from 240° to 250° K. Thomsen's value obtained from essentially the same material was 221.5. Petersen finds in this difference ground for the assumption that there are two different soluble vitreous forms of selenium. It is much more likely that these variations are experimental, especially since Petersen has himself shown that vitreous selenium always contains more or less of the metallic modification.

From the monoclinic red crystals which separate out of carbon disulphide, Petersen finds the heat of formation of the chloride Se_2Cl_2 to be 207.5 K. From Thomsen's data, using this value, we obtain for the heat of formation of the oxide SeO_2 from the monoclinic form, 562.0 K. Deducting this from 572.5, Thomsen's result for the oxidation of amorphous selenium, we get 10.5 K as the heat of transformation of that form into the red crystalline. By a direct comparison of the results for the heat of formation of the chloride from monoclinic and vitreous selenium we find quite a different value; but they both point at least in the same direction, that the heat value in the change from liquid selenium to monoclinic red, is positive.

Metallic selenium was prepared by Petersen by heating the element to 250°, then cooling to 180°, maintaining this temperature for a long time, and then slowly cooling. So prepared, it contains about one percent of soluble selenium. The value for the heat of formation of the chloride Se_2Cl_2 from this form is 200.0 K, and for the crystals from selenide solutions 199.8 K. This gives, by calculation, for the heat of formation of the oxide SeO_2 from metallic selenium, 558.2 K, a value which differs by 14.3 from Thomsen's result for the amorphous form. It should be mentioned that Petersen, in quoting Thomsen's data, makes a correction of 9 K in them for the heat of solution of SeO_2, as Thomsen's results refer to reaction in solution. Summing up the results thus far obtained, we have for the heat of transformation of liquid into metallic selenium:

Regnault (direct)	15 K
Fabre (direct)	55
(indirect)	57
Petersen (indirect)	14.3

For the change from the amorphous to the vitreous form we have the very doubtful value deducible from Thomsen's results, 3.5; and for the transformation from that form to the red monoclinic, 10.5.

8. The specific heat of selenium

Determinations of the specific heat of liquid selenium at any temperatures above 60° necessarily give uncertain values because of the danger of some of the element going over to the crystalline form. The heat set free in this transformation has so large a value that the change of even a very small quantity would utterly falsify the results. The determinations of the specific heat of the crystalline form are not open to this objection, provided the transformation into this form has been effected completely.

The data regarding the specific heat of the different modifications of selenium are to be found in the papers of Regnault (1840 and 1856), Neumann (1865), and Bettendorf and Wüllner (1868). Regnault's first determination was undertaken with some material which showed no appreciable sulphur content, but which was not tested for tellurium; nor are any particulars given as to how the material was treated before the determinations were made. The values, when compared with later results, show that he had in hand here, in all probability, the gray metallic modification. The two forms were not well differentiated at that time. Regnault made three determinations, and found for a range of temperature from 98° to 12°, the values:

0.08349, 0.08396, 0.08368; mean 0.08371.

Sixteen years later he returned to the subject. This time he made himself familiar with the change from the vitreous to the metallic form. An analysis of the material gave Se 97.75 pct, Te 2.25 pct. Here again we have no information concerning the preparation of the material, but are told merely that it was metallic selenium. The results for a range from 98° to 20° are 0.07517, 0.07563, 0.07675, 0.07709; mean 0.07616. The method used by Regnault in both of these investigations was the ordinary calorimetric one, by heating the substance to a higher temperature, dropping it into a large mass of water, noting the rise in temperature, and correcting for the alteration in this rise due to radiation and to the cooling effect of the surrounding atmosphere.

A determination with vitreous selenium between 87° and 19° gave the results:

0.1036, 0.1026; mean 0.1031.

At lower temperatures the values were as follows:

Vitreous form	−27 to +8°	0.07461
	−20 to +7°	0.07476
	mean	0.07468
Metallic form	−20 to +7°	0.07323
	−16 to +7°	0.07570
	mean	0.07446

Thus at low temperatures the specific heat appears the same whichever form we have in hand. These results show a large variation from the earlier ones of the same author; it is unfortunate that no information is given regarding the preparation of the material; there are not even sufficient data to make possible a recalculation of the results.

In the light of his earlier values, and of the later work which we shall have to consider below, there can be little doubt that the specific heat of metallic selenium is about 0.084, a value which varies widely from the above. It is difficult to imagine that Regnault by any error used vitreous in place of metallic selenium in the later determination; on the other hand, it is possible that he was here dealing with the red crystalline form; true, the direct production of this modification from the vitreous has never been observed with certainty, but it is not in the nature of the case impossible; and there are other isolated instances on record where the assumption of such a change is at least a convenience.

The next specific heat determinations are those made by Neumann, in Göttingen, in 1865. The method used was Regnault's. His experiments were confined to the metallic form which, it is to be inferred, was prepared by heating vitreous selenium in the water-bath. As a mean of thirteen determinations, varying from 0.0847 to 0.0872, he finds the value 0.0860. Neumann used an arbitrary thermometer, but the range over which he worked was from the temperature of boiling water down to about 21°.

Finally, in 1868, Bettendorf and Wüllner published the results of their determinations. They followed essentially the same method as Regnault, simplified in certain details according to the procedure of Kopp. Their statement that Regnault prepared his material by heating the red powder obtained from selenious acid solutions finds no support in Regnault's original papers. Furthermore, their conjecture that Neumann worked with a mixture of two forms is unnecessary. It is based on the abnormally low value for the specific gravity of Neumann's material, but this is shown elsewhere to have been most probably due to experimental error.

Metallic selenium. Bettendorf and Wüllner prepared their material by heating amorphous selenium in an air-bath at 100° for a week. The substance was then gray in color, and had the specific gravity 4.797. Their values are:

0.0840, 0.0839, 0.0846, 0.0841, 0.0828, 0.0850,
0.0870 0.0829, 0.0825; mean 0.0840;

the range of temperature being from 60° down to 25°.

A second specimen prepared in an entirely different way gave the same result: The material in this case was the crystals which separate from solutions of selenides of the alkalies on standing in contact with the air. The following values were obtained: 0.0842, 0.0838, 0.0836, 0.0847, 0.0835; or in the mean 0.08399, the range of temperature being the same as before.

Vitreous selenium. The material was prepared by dropping melted selenium into cold water; since vitreous selenium softens at 40° to 50° the determinations were restricted to temperatures below 38°. The results are as follows: 0.0952, 0.0958, 0.0950; mean 0.0953, the range of temperature being from 38° to 20°. For higher temperatures, the following results were obtained:

Temp.	Spec. heat
53–22°	0.1104
62–20°	0.1147

There is a possibility that these large values may be due to a certain amount of the selenium having gone over to the metallic form. They could be checked by making a determination in the reverse way, i. e. by introducing the cold substance into a hot bath; here, if any such change went on, the values would come out too low.

The above results are, in summary, as follows:

Vitreous selenium

Temp.	Spec. heat	Observer
87 to 19°	0.1031	Regnault II
−25 to + 8°	0.0747	——
38 to 20°	0.0955	B. and W.
53 to 22°	0.1104	——
62 to 20°	0.1147	——

Metallic selenium

Temp.	Spec. heat	Observer
98 to 12°	0.0837	Regnault I
98 to 20°	0.0762	Regnault II
−20 to + 7°	0.0745	——
100 to 20°	0.0860	Neumann
60 to 25°	0.0840	B. and W.

Person[1] determined the specific heat of ordinary bees' wax, a substance which, like vitreous selenium, gradually softens on being warmed. His results are:

Temp.	Spec. heat
−21° to 3°	0.4287
6° to 26°	0.504
26° to 42°	0.82
42° to 58°	1.72

9. Specific gravity determinations

The difficulty in determining the specific gravity of selenium lies in the fact that even the smallest particles of it may contain air cavities; so that it is usually necessary, in order to get satisfactory results, that the material shall be in a state of fine powder and that it shall be subjected to exhaustion. The easiest way to effect this is to cover the powder with some of the liquid used for filling the specific gravity bulb, place this in a desiccator, and pump out. The liquid used may be alcohol or benzene. It is to be noted that when alcohol is used, it is best, if the liquid be not pure, to pour off that part of it which has stood over the

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[1] Ann. [3] 27, 263 (1849).

selenium when exhausted, since it may have suffered a change of density due to the vaporization of the more volatile component.

The determinations recorded below were all made at 25° in a specific gravity bottle of capacity 50 cc. This was left in a bath at constant temperature for fifteen minutes. In order to test whether this was a sufficient time, the bottle was replaced in one instance, after weighing, and left in the bath for two hours longer; at the end of that time the difference in weight was only 1 mg. The bath used was an ordinary Ostwald thermostat provided with a thermo-regulator of the usual size, but filled with toluene. This forms an instrument of a very high degree of sensitiveness, so that it was possible to keep the total variations in temperature within 0.01° for hours at a time.

It was found better to dispense with the usual stopcock where toluene was used; this was done by altering the gas-entry tube as indicated in the accompanying figure. (Fig. 3.) The tube *a* is partly filled with mercury, and when the desired temperature has been reached, is slipped over the end of the drawn-out tube, and held in place by a cork tied on to the neighboring upright. The rest of the piece is arranged in the usual manner.

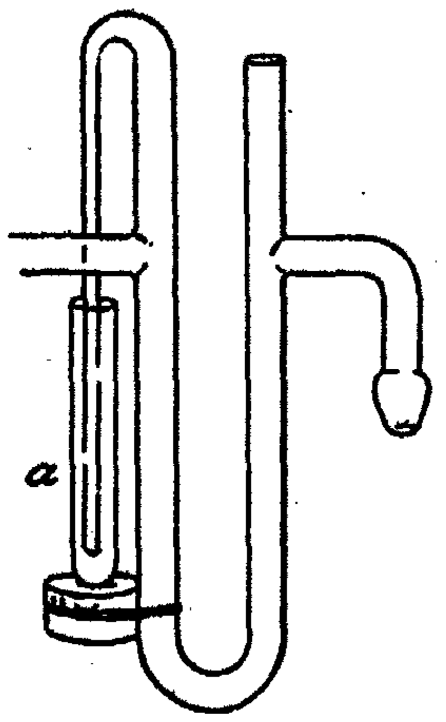

Fig. 3

An attempt to use the floating method with amorphous selenium failed. The double nitrate of thallium and silver[1] gives a liquid of sufficient density, but selenium is at once acted upon by it.

The specific gravities of the different forms of selenium have been very often determined, and sometimes with widely varying results. The variations have been, in the main, due to the difficulty mentioned above. When the element is present in fragments, these contain air cavities which render specific gravity determinations quite hopeless.[2] The only method by which uniform results can certainly be obtained is to powder the material and then exhaust for some time, best under the liquid in which the density is to be determined. This liquid should not be water, because it does not readily wet any one of the modifications of selenium; alcohol has been used in all of the more careful determinations.

Berzelius (1818), who had observed the change from the vitreous to the gray form, records the specific gravity of the former at

4.3 — 4.32,

and says that the transformation into the gray form causes no change of density.

The next data are those of Schaffgotsch (1848), who recognized the difficulties to be encountered and avoided them by making the weighings in alcohol and exhausting to get rid of the adhering air. He found at 20° for vitreous selenium, 4.276 to 4.286; for metallic selenium, prepared by heating to 250° on a sand-bath, and very slowly cooling, 4.796 to 4.805; and for the amorphous red form, 4.259 to 4.269.

Hittorf (1851) determined the density of the crystals which separate from solutions of selenides of the alkalies, and found the value 4.808; he gives no information regarding his method of determination.

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[1] Retgers. Jahrb. f. Min. 1893 and 1896.

[2] The same kind of difficulty is encountered in determining the specific gravity of tellurium. See Lenher and Morgan. Jour. Am. Chem. Soc. 22, 29 (1900).

In 1853, Schaffgotsch returned to the subject and made a series of more elaborate determinations.

I. Vitreous selenium, prepared by rapid cooling, from the fused element:

Four determinations with fragments which proved afterwards to contain air cavities, and with powder which, although boiled with water, was not rendered free from air, gave values varying by but little from 3.9. The powder, on being boiled, must certainly have gone over to the metallic form, yet Schaffgotsch records the density observed in this case as 3.9267; which goes to show how large the errors due to air cavities may be, and, particularly, the importance of choosing an appropriate liquid in which to work.

A second series, carried out with fragments which were not investigated with regard to enclosed air, gave 4.259 to 4.269.

The third series was made with air-free vitreous selenium (Schaffgotsch appears to have satisfied himself of this by inspection only), and with powder which was freed from air by repeated exhaustion under water or determined in alcohol, which, the author says, renders the use of the air-pump unnecessary. The results are very concordant, varying only from 4.276 to 4.286; or, in the mean, 4.281.

II. Metallic selenium, prepared by melting and then very slowly cooling, gave, when powdered and determined under alcohol, values which varied in four determinations, between 4.796 and 4.805.

III. Amorphous selenium — selenium blood as Schaffgotsch calls it — gave varying results, from 4.245 to 4.275. After causing it to coagulate by heating to 50°, the results ran from 4.250 to 4.277, thus showing no difference from the powder. These last determinations were made in water. Schaffgotsch considers that, in view of the difficulties of the determination, the results are to be considered as indicating a density identical with that of vitreous selenium. The material was prepared by the addition of hydrochloric acid to a solution of selenium in sodium sulphite.

Mitscherlich (1855) studied the two red forms which separate from carbon disulphide solutions and found their specific gravity to be 4.46 to 4.51. He seems to have taken the two forms as being identical except in crystal habit, and his density determination was possibly made with a mixture of the two. He states that it was possible by heating them to 150° to transform them into the gray modification, whose specific gravity he found to be 4.7. The determinations were made in alcohol at 15° and without powdering the material. The crystals which separate from selenide solutions had a density, according to Mitscherlich's results, of 4.76 to 4.79. Both of these forms — the black crystals as well as the gray material obtained from the red crystals at 150° — he therefore considered to be identical with the ordinary gray selenium whose density Schaffgotsch had found to be 4.80.

Neumann (1865) made a determination of the specific gravity of metallic selenium, and records the density of this substance "in fragments" as 4.41. This value, lying as it does so far below 4.8, suggested the possibility of there being a second form of gray metallic selenium, and most of the modern textbooks describe two forms. The only further confirmation of this view is supplied by the experiments of Rammelsberg (1874) which will be found discussed below.

The next density determinations were those of Bettendorf and Wüllner (1868), who were also engaged upon the question of specific heat. The only value they give is for a sample of red amorphous selenium, which had been heated for a week in a steam-oven, and had at the end of that time a density of 4.797 at 20°. No details of the work are given, but it is obvious that they had in hand the gray form. The accuracy of the value found is due to the fact that the material, being obtained from the red powder, was already in a state of fine division, and hence no considerable error from air cavities should enter in. We come then to the paper by Rammelsberg (1874). The discrepancy between the results of Neumann's observations and those of earlier investigators seemed, to Rammelsberg, to call for a redetermination of the specific gravity of all the various forms of selenium. His determinations were made partly in alcohol, partly in water; but it does not appear that the material was powdered, nor that the air-pump was used, except perhaps in the determinations under water.

The amorphous variety obtained by the reduction of selenious acid in solution, by sulphur dioxide, gave values between 4.27 and 4.34, while melted selenium, i. e. vitreous, gave 4.29 to 4.36. The crystals obtained from carbon disulphide, which are described as brownish red and transparent, were subjected to a large number of separate determinations in alcohol; only small quantities of the crystals were used, and with very variable results, the mean values of which are given as

4.418 — 4.54 — 4.59,

i. e., about the same as Mitscherlich had found. For the crystals which separate from selenide solutions the figures given are

4.77 — 4.79 — 4.86.

But the most interesting values are those which Rammelsberg found for the gray metallic selenium which he prepared by heating the vitreous form to 120°–150°. The product is described as insoluble in carbon disulphide and it may therefore be assumed that it contained no considerable quantity of the vitreous form unchanged. The results for determinations made partly in alcohol and partly in water, are

4.437 — 4.464 — 4.487 — 4.545 — 4.563 — 4.590,

or, in the mean, 4.514. One would have thought that the extremely large variation in these results would have aroused Rammelsberg's suspicions as to their value; but apparently not. He remarks merely that they all lie very much nearer to Neumann's value, 4.4, than to Schaffgotsch's of 4.8, which is not the case. Neumann expressly states that his figure referred to selenium "in fragments," and Rammelsberg leaves the same to be inferred regarding his, whereas Schaffgotsch's determinations were made with powdered material. I made an experiment to find what difference would be observed in the density of the same material in fragments and in powder. To this end, about two grams of vitreous selenium were heated for an hour at 120°–150°. The product was entirely gray, and the fracture had the same color; no trace of the red form could be observed in it. The determinations were made in alcohol at 25°. The first was made with the material broken up only enough to allow of its being brought into the specific gravity bottle. The value found was 4.55. The selenium was then taken out, dried and powdered, replaced in the bottle, covered with alcohol, pumped out for half an hour, and then re-determined. The new value was 4.77. In view of these results there can be little doubt that both Rammelsberg and Neumann had in hand ordinary metallic selenium, and that the variations from the true value 4.8 displayed by their results, are due to experimental error. This view is confirmed by the fact that Neumann found the same value for the specific heat as did Bettendorf and Wüllner, while these authors found 4.797 for the density of their material. As a further illustration of the extent to which error of this kind is possible, attention may again be called to the remark of Berzelius that the change from the vitreous to the metallic form causes no change whatever in the density (4.3). The accuracy of Rammelsberg's results with the other modifications is due to the fact that these forms having separated from solution, do not contain air cavities.

A number of density determinations were made by Petersen (1891), who prepared metallic selenium by heating the vitreous modification to 250°, then cooling to 180° and keeping it at that temperature for a long time; finally the material was slowly cooled. It was found to contain about one percent of soluble selenium. The density determined at 17°–18° was found to be 4.63 (4.62–4.64). The explanation for this very low value is to be found in the fact that the determinations, though carefully made, were carried out in water, which has always yielded unsatisfactory results with this form of the element. We have seen that Schaffgotsch obtained in this way a value as low as 4.39. The method of procedure used by Petersen was to bring the substance into the pycnometer, cover with air-free water, warm, place under the pump, and pump out until the water was caused to boil. That author drew from his result the conclusion that specific gravity cannot be taken as a criterion for the crystalline forms of selenium. But this conclusion hardly seems called for, considering that all determinations carried out with alcohol under appropriate conditions have yielded, for the metallic form, values which lie very near to 4.8.

The monoclinic red crystals obtained by extraction of amorphous selenium with carbon disulphide, yielded, by the same method as above, the values 4.44–4.47. When compared with Mitscherlich's results, which are, as before pointed out, not free from possible error, this gives as the most probable value for the density of monoclinic red selenium, a figure not differing by much from 4.47.

It will be noticed that all accurate determinations of the densities of amorphous and vitreous selenium yield results indicating a slightly lower value for the amorphous form. The following are the data on the subject:

	Amorphous	Vitreous
Schaffgotsch (1848)	4.259–4.264	4.276–4.286
——— (1853)	4.245–4.275	4.276–4.286
Rammelsberg	4.27 –4.34	4.29 –4.36

The difference is so slight as to be quite within the limits of experimental error, and the observers themselves have generally attributed it to that source; yet its constant recurrence, always in the same direction, leads to the conclusion that the two forms may really possess slightly different densities, although representing one and the same modification of the element. If this is so, the difference is due to the fact that the material exposes in one case a maximum, in the other a minimum of surface; for the amorphous form, which gives colloidal solutions with water when freshly precipitated, is in a state of extremely fine division. It is quite possible that the difference in the state of aggregation should cause a difference in density as well as in other properties of the substance. Any experiments made with selenium itself with the idea of establishing such a difference would be rendered inconclusive by the possibility of the formation of a small amount of metallic selenium during the course of the experiment. It is, on the other hand, very easy to find analogous cases among the other elements; colloidal solutions have been prepared of gold, silver, copper, mercury, sulphur, and other elements, and all of these are obtainable in the form of impalpable powders, quite different in appearance from the compact material. Some experiments are now in progress to determine whether a measurable difference of density exists in such cases. This is not improbable if the idea suggested by van der Waals[1] be correct — that there is no discontinuous change between a liquid and the vapor above it; for if there is a film of intermediate density in the case of an ordinary liquid, and its vapor, it is entirely probable that solids would also have a bounding surface of lower density than the material within; equally so a viscous substance like amorphous selenium. Increasing the surface for a given weight of material would then always bring about a lowering of the density, and if the surface were made relatively very large, this lowering might become apparent.

Summary of specific gravity results

The most careful determinations which have been made of the specific gravity of the various forms of selenium lead to the following results for the different modifications, at ordinary temperatures:

Amorphous	4.26
Vitreous	4.28
Red crystalline	4.47
Metallic	4.80

Atomic volumes

Taking the atomic weight as 79.2, these values give the following atomic volumes:

Amorphous	18.6
Vitreous	18.5
Red crystalline	17.7
Metallic	16.5

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[1] Ostwald Lehrb. I, 540.

10. Conductivity of selenium. Action of light

Beyond a vague experiment of Knox (1839) there is no information of value regarding the conductivity of selenium before 1851, when Hittorf found that the vitreous form was a very good insulator, whereas in the metallic state the element conducts electricity fairly well, and furthermore shows an unusual property, in that, unlike typically metallic substances, but like tellurium, its resistance decreases with rising temperature up to the point of fusion; at that point it suddenly increases. Hittorf used carbon plates as electrodes in his experiments.

In 1873 Willoughby Smith announced that the resistance of selenium to the passage of electricity was diminished by light. We have no details regarding the preparation of the selenium, which was in rods 5-10 cm long, and 1-1.5 mm thick. They were, plainly, of the metallic modification, as the later correspondence shows, and were sealed in glass tubes, through the ends of which platinum wires were fused for the purposes of connection. Even the light of an ordinary gas burner was found to exercise a marked influence upon the conductivity, which rose and fell according as the cell was exposed to the rays of the burner, or shaded by interposing the hand. The difference with even so feeble a source of light as this amounted to 15 to 20 percent. "If the light be intercepted by rock salt or by glass of various colors, the resistance varies according to the amount of light passing through the glass. To ensure that temperature was in no way affecting the experiments, one of the bars was placed in a trough of water so that there was about an inch of water for the light to pass through, but the results were the same; and when a strong light from the ignition of a narrow band of magnesium was held about nine inches above the water, the resistance immediately fell more than two-thirds, returning to its normal condition immediately the light was extinguished."

These observations excited widespread interest and elicited some correspondence, which will be found in the volume of Nature for the year 1873.

Later in the same year, Sale presented before the Royal

Society the results of his researches, confirming the observations of Smith, and showing in addition that the part of the spectrum most active on selenium is just outside the red rays, at a place nearly coincident with the locus of the maximum of the heat rays. He showed further that the effect of light, on exposure, is instantaneous, but that on cutting off the light, the return to the normal resistance is not so rapid.

In 1874 Lord Rosse announced some experiments which he had made for the purpose of establishing that it was light and not heat which was the cause of the change. He compared the action of the selenium cell with that of a thermopile under similar conditions, and found no accordance between them at all. The non-luminous radiation from hot bodies had no action upon the cell, whereas the effect of candle light was not very materially diminished when allowed to pass through a plate of glass or a solution of alum.

Further confirmation of these results was supplied in 1875 by Siemens, who adds some very interesting information regarding the preparation of the cells. He found that no satisfactory results were to be obtained from material which had been transformed into the metallic modification by heating to 100° or 150°, but that by long heating to 210° or even by cooling melted selenium down to 210° and maintaining it at that temperature for some time, "another modification," as Siemens says, is obtained, and this shows a higher degree of conductivity as well as a normal behavior toward changes of temperature, the resistance rising as the temperature is raised. The action of light upon such material is also very much more marked, and entirely constant, the earlier cells having given variable results. Two flat spirals of platinum wire about 1 mm apart, between mica plates, formed the cell, and a layer of selenium was fused over the spirals so as to fill the interspaces. This formed a very sensitive instrument, and Siemens found that heat causes a diminution of conductivity, whereas direct sunlight increased it more than ten-fold, the increase being nearly proportional to the square root of the intensity of the light. In the same year appeared a paper by

Adams, bringing further confirmation of the statement that the light rays alone are active. He found that a marked effect was produced by the light of the moon, and that of the various parts of the spectrum the greenish-yellow rays were the most powerful.

Practical application of these new properties of selenium was now made in the construction of instruments for the measurement of light intensities, etc. Thus in the year 1875 Siemens described his "Electrical Photometer", Bell his "Photophone" in 1880, Bidwell his "Telephotograph" in 1881, and so on. Since the construction of these instruments had added nothing to the theory of the matter in hand, a mere mention of them will suffice.

The year 1876 is rich in memoirs. Draper and Moss undertook to determine what they call the "precise molecular state" of light-sensitive selenium; but though they describe several forms of metallic selenium, which show varying behavior toward the electric current, nothing is said of the methods of their preparation.

Later, Moss made a study of the action of mercury vapor on rods of vitreous selenium and found that when these are allowed to stand over mercury, they acquire a film of high conductivity, no doubt selenide of mercury. The same result is obtained by dipping them into mercury. Rods of the metallic modification also show increased conductivity under like circumstances. Adams, in the same year, showed that the change in resistance of selenium under light stimulus is proportional to the square root of the illuminating power. Experiments with tellurium cells indicated a distinct though very slight influence of light upon their conductivity. Adams and Day then showed that there is a change of resistance when the direction of the current passing through a selenium cell is reversed. Their method of preparation of the cell was to fuse platinum wires against the ends of a rod of vitreous selenium and then place this in a bath of hot sand for some time. They showed, moreover, that, on the whole, there is a general diminution of resistance in the selenium as the battery power is increased.

Their results indicate that the conductivity of selenium cells is electrolytic. After passing the current for some time through the selenium, and then disengaging the electrodes from the battery and connecting them with the galvanometer, a current, sometimes of considerable intensity, was set up in the opposite direction, thus showing a polarization effect. Light has an action upon this polarization current; indeed they found that light is capable of setting up a current in such an arrangement even where no current has previously passed. The sensitiveness is different in different parts of the same piece of selenium, but in general the current is set up from the less towards the more illuminated regions. It is produced instantaneously and falls at once to zero when the light is shut off. When the light fell upon a junction, the current passed from the selenium to the platinum, through the junction.

A most important contribution to a knowledge of the subject was supplied in this year by Siemens. He endeavored, in the first place, to find other substances showing a behavior to light similar to that which is manifested by selenium, but in vain. Even in the case of tellurium, to which Adams had attributed this property, Siemens could find no distinct action which could not be explained as a heat effect.

In order to repeat the observation of Hittorf under better conditions, he prepared a cell with vitreous selenium and carbon electrodes. This was connected to a single Daniell cell and plunged into a bath of paraffin maintained at 280°. A thermometer standing in the centre of the cell showed the change in temperature in the mass of the selenium, and any differences in its conductivity were read off upon a galvanometer. The results are shown in the accompanying diagram (Fig. 4).

The curve A represents the temperature of the selenium, the curve B the conductivity, and C represents a normal change of temperature for the conditions of the experiment. Time is plotted on the horizontal axis and the values upon the vertical axis indicate temperatures for the A and C curves, and conductivities for the B curve.

Considering first, the A and C curves, we find that at about 100° where the transformation into the metallic form would naturally begin, there is an abnormal rise in temperature. This is due to the heat of transformation. On the other hand, when we come to about 220° there is a retardation because we have arrived at the melting-point; after complete fusion, the two curves run together again. Consider now the A and B curves. Siemens records that at 80° there was still complete non-conduction; when the thermometer had reached 162° the deflection of the galvanometer had risen to 870 scale divisions; plainly by this time a good deal of the material had gone over into the metallic (conducting) state. At 200° the deflection was 1520, but when the thermometer registered 215° it had fallen to 120 scale divisions. The thermometer, being in the middle of the mass, shows a certain lag, so that this reading of 215° doubtless corresponds to a higher temperature throughout the mass, and the fall of conductivity is due to the fact that a good deal of the selenium had already passed into a state of fusion. At about the time that complete fusion is reached, the conductivity shows a minimum, and after that, with constant temperature, it rises gradually to the end of the experiment, the temperature of the selenium remaining at about 250° to the last. The conclusion drawn from these observations by Siemens, that metallic sele-

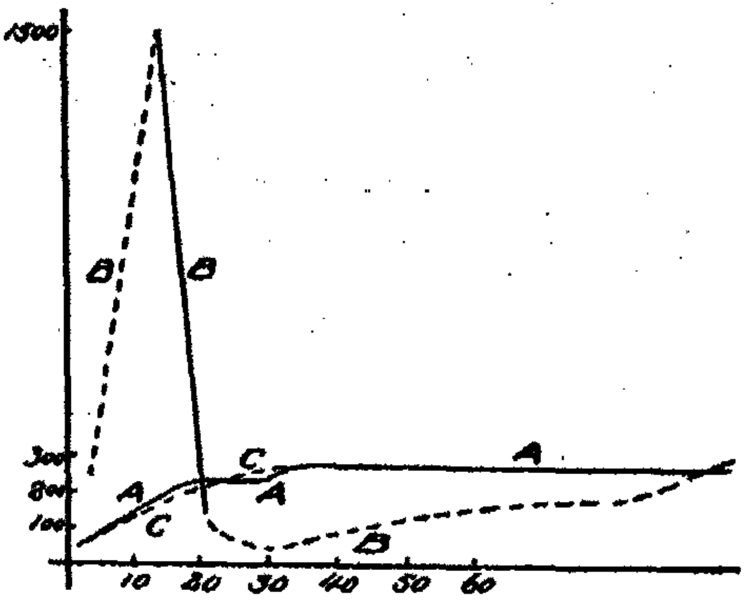

Fig. 4

nium shows increasing conductivity with rising temperature, rests on insufficient ground, because the entire period between the beginning of the experiment and the moment when the melting-point was reached was less than twenty minutes, and five minutes of this time were occupied in raising the temperature to 100°. During the remaining period, there was probably a continuous change going on from the vitreous to the metallic modification, which would, of itself, bring about an increase of conductivity until the change in this direction, in the cooler parts of the cell, was balanced by a change in the opposite direction, due to fusion, in the hotter parts.

Later experiments, however, showed that the conductivity of gray selenium does increase with rising temperature.

The gradual rise in the B curve is difficult to explain except on the ground of chemical action. Shelford Bidwell has shown, in a paper published somewhat later, that the peculiar behavior of selenium cells may be due to the formation of selenides. Such a reaction might easily go on in this case with the metallic impurities contained in the carbon electrodes; but of that more will be said later.

In another experiment, where the direct heat of a flame was used, Siemens found that the conductivity increased up to 350°, where rapid vaporization of the selenium set in.

The remark of Siemens that in the case of both solid and liquid selenium the conductivity decreases with continued heating, stands in unexplained contradiction with the results of the above experiment.

If the current be passed for some time, Siemens finds a diminution of conductivity as if polarization had set in, opposing itself to the passage of the current.

Experiments made with metallic selenium prepared by heating the vitreous form to 150° show that the conductivity does slowly fall when the temperature is kept constant, and also that a higher result is always obtained at a given point of temperature by cooling down to it, than by heating up to it.

Siemens passed next to the use of other electrodes, namely those of platinum and iron, having, as he says, satisfied himself that solid selenium did not attack these metals. Yet it will be seen that in all the preparations he used, it was not solid selenium alone which came into contact with the metals, but liquid selenium as well, and at high temperatures. The electrodes in these experiments were either in the form of spirals, or lattice work, so as to expose a maximum surface of contact with the selenium while permitting of full illumination. On the effect of changing temperatures, the following experiment is worth transcribing:

Two cells, numbered 33 and 36, were placed in a paraffin bath, whose temperature was then rapidly raised to 200°. Both cells began to conduct at about 100° and reached a maximum at 200°. Cell No. 33 had then a conductivity of 2720, No. 36 of 2120, in arbitrary units. The temperature was maintained for four hours.

The change with the time is shown in the table:

Time elapsed	Cond.	
	No. 33	No. 36
1 hr	1240	940
2 hr	1090	820
4 hr	1000	800

No. 36 was then rapidly cooled, and No. 33, being slowly cooled, gave the following readings:

Temp.	Cond.
180°	1020
150	2460
130	5730
120	8320
100	17020
80	21280

after which it diminished. On the following day it showed, at ordinary temperatures, a conductivity of 6190. Meanwhile No. 36 when suddenly cooled to room temperature, had been found to have a conductivity of 16450; after half an hour, of 14330; and on the following day 7710.

Thus these cells show a decreasing conductivity, when maintained at 200°, but when cooled down, whether slowly or rapidly, the conductivity rises rapidly. This is in direct opposition to the results obtained with metallic selenium prepared in the ordinary way. The difference in preparation is that the "ordinary" form is made by heating vitreous selenium to 150°, whereas this form is produced when the same material is heated to 200°. But it must be noticed that the experiments on the other form were made with quite a different kind of cell, provided with carbon poles. The cell in these later experiments, by exposing so large a surface to the selenium, increases very much the possibility of a marked influence due to the formation of selenide at the surfaces of contact.

Bellati and Lussana[1] have measured the conductivities of metallic selenides and they find that, in general, these compounds show increasing resistance with rising temperature; i. e., they conduct like metals. Furthermore, they find, in the case of copper and silver selenides, curious breaks in the curves at higher temperatures. It seems, therefore, not at all improbable that the change in selenium cells by long heating at 200°, which causes them to conduct metallically, may be explained by the formation of selenides.

Siemens finds that a cell which is only heated for a short time to 200° does not behave differently from one containing the ordinary metallic modification. In order to give to the cells the property of metallic conduction, it is necessary that the selenium should be first in the vitreous state, and that this should then be heated directly to 200°. If it has first been heated for some time at 100° and the temperature subsequently raised to 200°, the effect is either not produced at all, or to a far less degree. Nor does selenium which has been melted and cooled

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[1] Att. Inst. Veneto (6) 6, 189 (1887), or Ostwald's Lehrbuch, II, 2, 422.

to 210° and then maintained at that temperature, display any abnormal behavior. It conducts like ordinary crystalline selenium.

Now vitreous selenium when heated to 200° is quite soft, and would be much more likely to attack metallic surfaces than the crystalline form, so that it is natural to suppose that in so far as the formation of selenide may be responsible for the behavior of these cells, the method of heating adopted by Siemens would be most likely to produce the effect desired. By heating at 100° the mass would be almost entirely transformed at a temperature where it would be much less likely to act on the metals, and we would not expect to find any very marked reaction on heating this then to 200°.

But the second observation of Siemens recorded above, regarding the failure to prepare cells by cooling down fused selenium to 210° is, as he himself points out, in contradiction with his earlier experiments in the same direction, and it is certainly not plain why this method of preparation should not bring about as good results as the other.

From the remaining experiments reported in this paper, the following conclusions are drawn: The observation of Adams that the conductivity of selenium cells increases for higher electromotive forces, is confirmed for such cells as have been prepared by heating vitreous selenium at once to 200°, but not for those where the transformation has been effected at lower temperatures. The effect of a continued passage of a current through a cell is the same as if a heating were thereby produced, i. e. for one kind of cell it causes a rise, for the other a fall in conductivity. The change is shown not to be due to temperature. Reversing the current brings about such various phenomena that no general statement can be made about them. In some cells there is no effect at all; in others, evidence of a polarization current.

With the cells prepared at 200°, if the heating at that temperature has been sufficiently long continued, so that the conductivity has attained a constant value, then when the temperature is lowered the conductivity shows an immediate rise. If the heating was less protracted the conductivity falls at first with falling temperature, reaches a minimum, and then rises again. The position of this minimum on the scale of temperature is dependent upon the length of the previous heating.

"Selenium shows an extraordinary behavior on change of temperature. It assumes a new conductivity value at once when the temperature is altered, and this change for rising temperature is in the direction of higher conductivity, if the selenium is of the first form (ordinary metallic), lower conductivity if it is of the second (prepared at 200°). But the new value does not remain constant. For the second form, it falls after every change of temperature, no matter whether this change be up or down, and approaches a limiting value, slowly at first, then more rapidly. The farther below the turning point (minimum, see above) the new temperature lies, the greater is the conductivity which is at first manifested, but the more rapid also is its diminution. If the selenium has been maintained for some time at a lower temperature so that its conductivity has fallen to a minimum, the peculiar phenomenon may be observed with the second form, that a rise of temperature brings with it at first an increase of conductivity. This is followed by a fall, and the end value is of course less than that for the lower temperature."

Cooling to —15° destroys the peculiar properties of the second form and converts it apparently into ordinary metallic selenium.

Siemens noted the influence of the size of the surface of the electrodes on the behavior of the cell, and also the importance of uniform contact between the selenium and the metal.

In explanation of the extraordinary behavior of the element, he assumes that a third form is produced by continued heating at 200°, that this form is only stable at that temperature, and is at lower temperatures prevented from complete decomposition by being dissolved in, or combined with, ordinary metallic selenium. This view offers an explanation of the turning point, beyond which the character of the conduction changes from metallic to electrolytic, and also of the fact that the cells show such a remarkable lack of uniformity of behavior with changes of temperature.

That this assumption of a second form of metallic selenium has met with no support in my own experiments, has been shown above. Whether it will be possible to clear up all of Siemens' results by a further study of the influence of selenides upon the conductivity of selenium cells, must remain for the present an open question. Meanwhile, it is to be remembered that many of the irregularities which he noted may have had their seat in changing and irregular contact between selenium and metal; the cells were prepared with vitreous selenium, and when this goes over to the metallic form, there is, as we know, a very considerable diminution in its volume; this would tend to cause rupture at any surface of contact as well as to introduce air cavities everywhere through the material.

Lenher and Morgan,[1] in their experiments on the conductivity of tellurium, found that alterations in the contact between the material and the electrode used, caused the widest variations in their results. Indeed the best values they could get are very far from uniform.

In the year 1877, there appeared a second paper by Siemens, devoted to a more detailed consideration of the action of light. He finds the greatest activity in the red region of the spectrum; concludes that there are too many disturbing influences in the measurements to make it possible to find any fixed relationship between the light intensity and the resulting change of conductivity; and, finally, presents some detailed experiments on the effect of continued illumination upon the cells.

At the same time, Forssmann announced the results of some extended experiments upon the action of light of different colors. His first results go to show a maximum effect in the red and yellow, a minimum in the green; but he found indications later on, that even invisible rays may produce an effect. For instance, lamp-light which had passed through a

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[1] Jour. Am. Chem. Soc. 22, 28 (1900).

solution of chromic chloride had a larger effect than the direct light itself, although the color of the chromic chloride was so intense that it was opaque to the eye even in direct sunlight. Other salt solutions were studied as well, but no general conclusions could be drawn from the results.

In the following year (1878), Sabine published a paper on "some electrical experiments with crystallized selenium" in which he brings out very clearly the enormous importance of the junctions in the behavior of selenium cells. "A large portion of the observed resistance of a so-called selenium resistance may, and frequently does reside in the junctions and not in the selenium." The same is shown to apply also to the alterations brought about by inversion of the current. Light and heat appear from his experiments to act in the same way upon the conductivity of selenium surfaces; and, finally, the alterations brought about by these means, are shown to be probably in the nature of an actual change in resistance, rather than, as some investigators have supposed, an electromotive force set up in the selenium in the same direction as the battery current.

Alexander Graham Bell, in 1880, presented an account of his practical applications of the selenium cell in the construction of the photophone. He found that "brass, although chemically acted upon by the selenium, forms an excellent and convenient material. Indeed, we are inclined to believe that the chemical action between the brass and the selenium has contributed to the low resistance of our cells by forming an intimate bond of union between the selenium and the brass." There is but little of theoretical interest in the paper, except that Bell finds the long heating and slow cooling formerly recommended in the preparation of selenium cells, to be unnecessary; this is probably because selenium acts more rapidly upon brass than upon platinum.

Obach (1880) found that phosphorescent light caused a change in the conductivity of selenium. The phosphorescent material used was of unknown composition, but being a commercial article was probably one of the alkaline earth sulphide preparations. Its action was relatively slight, yet distinct. Strangely enough, it was entirely cut off by the interposition of red or yellow glass, while blue glass transmitted six-sevenths of the original effect.

There is through these years a large amount of literature on the applications of selenium cells, scattered through such journals as Naturé, the Journal of the Society of Telegraph Engineers, etc. I have been at no special pains to collect references to such letters and short communications except in the cases where some fact of theoretical importance has been brought out. The best general account of this side of the subject will be found in Bell's paper cited above.

Kalischer's article in 1881 under the title of "photophone without battery," describes his attempts to produce a photophone in which the current was supplied by the electromotive force of the selenium preparation itself under illumination.

Moser (1881) records some very interesting observations on the nature of the contact between selenium and metals: "On a copper plate I melted amorphous selenium and put on it a second metal plate of zinc or copper. Then I heated gradually so that the selenium became crystalline; and I then annealed it. Whilst the amorphous selenium adheres very well to the metal plates, these cells proved very brittle when the selenium was crystalline. The selenium always split off from the copper plate. .... Every lamina which split off was on the upper side light gray, and on the lower side blue black, not brilliant, but dull. In the same way, the copper plate had now a similar dull blue-black covering. This blue-black body is cuprous selenide. ... This experiment shows that between the copper and the selenium, or rather the cuprous selenide, there is only a slight and imperfect contact."

The view advanced by Moser that "selenium is heated by light" and that the changes in its conductivity are produced through the expansion of the mass of selenium and consequent tightening of the contacts was disproved by Shelford Bidwell in 1883. We have seen too that experiments made some years previous had shown that the peculiar action of selenium cells could not be explained as a heating effect.

Fritts, in 1883, described the preparation of selenium cells of hitherto unattained sensitiveness and of very low resistance. One of them showed fifteen times as high a resistance in the dark as it had in ordinary diffused daylight of the room. He finds that the best metals to use are "brass, zinc, or iron or copper thinly coated with tin". (Apparently only the copper was tin-plated.) The properties of these cells are in other respects also, quite unusual. It is found, for example, that the kind of battery has a great deal to do with the result; thus some cells which were light sensitive when operated with a Leclanché battery gave no results at all with a bichromate battery. The effect of rapidly alternating currents was in some cases to reduce the resistance of a cell from many thousands of ohms to almost nothing; in other cases to raise it from next to nothing up among the thousands. These extremely variable results are left quite without explanation.

Fritts describes, in the latter part of his paper, the preparation of a new modification of selenium. The method of preparation is only imperfectly indicated, but seems to be by prolonged heating of selenium on a brass plate (to what temperature?) and then gradually cooling, under pressure. "The plates so made have portions which are transparent, situated apparently where the temperature was highest. The remaining portions of the plates are black and red, interspersed with gray. Thus upon one plate may be seen selenium in four different states or colors. . . . A small portion of the transparent selenium having, perhaps, one-half square inch of surface, had a resistance of only three ohms. It was found to be affected by light very little, if at all."

This transparent film which he considers as a new modification of the element, was perhaps in reality a film of fused selenide; or, it may have been a thin film of vitreous selenium, which is almost colorless in very thin layers. In the latter case we must assume an experimental error in the measurement of its resistance.

Selenide of zinc is described as a reddish-yellow substance. It is possible that this may have been the transparent material observed by Fritts.

In 1884, Bidwell, in a short article on the resistance of sulphur and selenium cells, showed that sulphur also gives light-sensitive cells when it contains sulphide of silver, and that selenium which has never come into contact with a metal possesses a resistance enormously higher than the ordinary material in the selenium cell. In a longer article, in 1885, the same author puts forward the hypothesis that the peculiarities of the selenium cell are really due to the presence of selenides. If this is the case, then the conduction may very well be electrolytic and would lead to the deposition of free selenium at one electrode and of the metal at the other. A change of this kind in the nature of the contacts might easily give all the remarkable irregularities in the behavior of selenium cells which have been recorded as the results of (1) a steady passage of the current, and (2) a reversal of its direction.

Kalischer (1887) studied the conditions under which the selenium cell becomes, as that author says, photoelectromotive. The cells have the ordinary form, but are constructed of two different metals, the selenium forming a connection between them. Copper and zinc were found to be a very efficient pair. They have, as a rule, a comparatively high resistance. "Besides the copper-zinc combination, I have used also copper-brass, zinc-brass, and copper-platinum. In all of these, the direction of the current which is called forth by light, is the same as in the ordinary galvanic elements. Thus, for instance, from zinc through the selenium to the copper." Nevertheless the same results may be obtained, using only one metal for the electrodes, though the current is less marked in this case. With lapse of time, the cells lose their power, and this loss is coupled with a decrease in resistance.

It is in this direction that most of the more recent work on selenium cells has been done. Thus v. Uljanin (1888) and Righi (1888) have both made important contributions to our knowledge of the electromotive force of selenium in the light.

Righi (1889) finds further that a selenium cell constructed with electrodes of different metals, shows an electromotive force even in the dark.

Hesehus (1884), in a purely theoretical paper, discusses the different explanations which have been suggested for the abnormal conductivity of selenium, and favors the assumption of two metallic forms of the element — Siemens' idea.

Bidwell in 1891 carries on the argument in favor of the theory that the behavior of selenium cells is due to selenides. He shows that the " annealing " of the cell which has almost always been regarded as absolutely necessary to the production of good light-sensitive cells, would in reality lead to the formation of a film of selenide at the junction. The deterioration of the cells with age, he attributes to the gradual thickening of the layers of selenide at the expense of the free, badly-conducting selenium, and thus the resistance of the cells slowly falls. " At length the layers of selenide become so thick that the coatings upon the two wires actually meet and touch each other. Thereupon the cell is short-circuited; its resistance no longer depends upon the selenium, but upon the metallic selenide, which is a good conductor."

The deposition of free selenium upon the electrode in the form of a covering of red tufts was shown experimentally. This material is amorphous selenium which, as we know, is a good insulator; hence the alterations in conductivity produced by continued use of the cell may well be large.

Since the appearance of this paper of Bidwell's no great addition has been made to the knowledge of the subject. Siemens, in his important paper, advanced the theory of a second form of metallic selenium, produced at 200°. That is the only good explanation, other than Bidwell's, which has been offered. Now we have seen in the other sections of this paper that it has been quite impossible to get any direct evidence of the formation of a new modification of selenium at higher temperatures. Furthermore, even granting its existence, there are still very many of the recorded observations which cannot be explained satisfactorily on that ground. The hypothesis of Bidwell gives much more hope of an ultimate clearing up of all the known facts. We have seen that selenides are undoubtedly produced when selenium is heated in contact with metals; that those metals — copper and brass — which are the most efficient in yielding sensitive cells, are among the ones most readily attacked. Hence the presence of selenides is certain. Bidwell has shown that there is a deposition of amorphous selenium at the anode, which would hardly be the case if the conduction were not really electrolytic. This deposition may well be the cause of the extraordinary differences observed on the reversal of the current, etc. Selenides are known to be good conductors; unfortunately the action of light upon them has not been studied; but the fact that sulphur which contains silver sulphide displays the light-sensitiveness of a selenium cell supplies an argument by analogy, of considerable force.

Furthermore, Bidwell found that a silver leaf placed upon glass and painted over with a solution of sulphur in carbon disulphide, if only partly shaded from the light, became, after fifteen minutes, dark brown in the illuminated part, while remaining whitish yellow where shaded. It may be mentioned here that Schuller (1883) found that when selenium is distilled there is a residue left containing copper and lead; this indicates that the commercial material is probably always more or less contaminated with metals.

It has recently been announced (1900) by Perreau that the resistance of selenium cells is reduced by X-rays, in the same way as by light.

So much of the time spent in the study of selenium cells has been devoted to the devising of instruments which have in the end proved inefficient that, in spite of the large literature of the subject, very few really scientific observations are on record. By beginning now with a methodical study of the behavior of selenides, and of selenium and selenide mixtures of known composition, there is every hope that a conclusion might be reached which would set the whole matter on a firm basis and supply moreover an interesting chapter on the action of light on chemical compounds.

10. Coefficient of expansion

Fizeau (1869) gives the value for the linear coefficient of expansion for vitreous selenium as 0.0000368. It is to be inferred that the experiment covered a range of temperature from 10° to 80°, and the value given above represents a mean result for 40°-50°.

Spring (1881) made a determination of the cubical expansion of selenium in the crystalline (metallic) form; the results are given below; the first series refers to the powdered crystals; for the second, these were subjected to a pressure of 6000 atmospheres, to get rid of air cavities. s is the specific gravity, β the mean coefficient of expansion from 0° to t°.

	t	0°	20°	40°	60°	80°	100°
I	s	4.7312	4.7176	4.7010	4.6826	4.6623	4.6396
	$\beta.10^7$	——	1478	1635	1743	1857	1981
II	s	4.7994	4.7869	4.7699	4.7526	4.7351	4.7167
	$\beta.10^7$	——	1307	1539	1644	1803	1751

It will be noticed that the specific gravity in each of these cases is somewhat less than the value to which the best of the other determinations have led. Spring's method was that of the weight thermometer filled with water; hence it would not be surprising if the material contained noticeable air cavities; this would explain the higher results for the uncompressed selenium.

VI. GENERAL PROPERTIES OF THE ELEMENT

1. Atomic weight

The first determinations are those of Berzelius (1818), and his results have only been confirmed by the latest and most accurate experiments. He found that 1 gram of selenium gave, when treated with chlorine, 2.79 grams of $SeCl_4$. This gives the atomic weight as 79.2 ($Cl = 35.45$). As a control experiment the chloride was transformed into the acid H_2SeO_3, and the hydrochloric acid thus liberated determined by silver nitrate. The chloride obtained from one gram selenium yielded, in this way, 7.2285 grams silver chloride, from which we calculate the value 79.35.

Berzelius did not, as Ostwald[1] states, lay the greater emphasis on the first value; on the contrary, he gives as the most probable result, the mean of the two, but he does state that of two such double determinations which he made he considers the first as the better, because it was made with the larger quantity of material. By another method he found that 1.888 grams of silver selenide, Ag_2Se, yielded 1.844 grams of silver chloride, from which the atomic weight is found to be 77.98 ($Ag = 107.9$).

The analysis of barium selenate quoted by Ostwald was not made as a determination of atomic weight. The same remark applies to the work of Mitscherlich and Nitzsch who made an analysis of selenic acid.

The next atomic weight determination is therefore that of Sacc (1847); in this case also several analyses of salts were made, which were recognized by that author as being unsuitable for atomic weight determinations. The methods upon which he laid stress were:

(1) The reduction of selenium dioxide by ammonium bisulphite and hydrochloric acid. This method yielded the results 78.3 — 78.2 — 79 ($O = 16$), and

(2) The reduction of barium selenite by the same reagents, and weighing the mixture of barium sulphate and selenium which is precipitated. This is a less accurate method, and gave, as the mean of three determinations, about 78.6.

Erdmann and Marchand (1849) analysed mercuric selenide and found that it contains 71.726 — 71.731 — 71.741 percent of mercury. These values give as the atomic weight 78.96, 78.96 78.93.

Dumas (1859) made a series of determinations in which he converted known weights of selenium into the chloride $SeCl_4$. His results vary from 79.2 to 79.66 and give as a mean value 79.46. As pointed out by Meyer and Seubert, Dumas has re-

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[1] Lehrbuch, I, 106.

corded in his article, in every case, the increase of weight as if it were the total final weight — i. e., what he calls the weight of chloride is really the weight of the absorbed chlorine.

Petterson and Ekman (1876) used two different methods:

(1) By weighing the silver obtained from silver selenite by heating, they obtained seven values varying between 78.90 and 79.18, and giving in the mean 79.01.

(2) By reducing weighed quantities of selenious acid by means of sulphur dioxide and determining the weight of the selenium precipitated, they found in five results a variation from 79.06 to 79.10; in the mean 79.08.

They consider the second method the more trustworthy and give the value 79.08 as representing most nearly the true atomic weight.

Finally, Lenher (1898) made a very careful study of the problem by the following methods:

(1) Silver selenite was converted into silver chloride; in this way, eleven results were obtained varying from 79.263 to 79.326.

(2) The silver chloride so obtained was then reduced in the case of eight of these, and gave values between 79.277 and 79.369.

(3) A weighed quantity of the bromide $(NH_4)_2SeBr_6$ was reduced by hydroxylamine and the resultant selenium weighed. Eight determinations gave values between 79.226 and 79.367. Lenher's mean values are:

From silver chloride	79.329 (eleven results)
From metallic silver	79.329 (eight results)
From bromide	79.285 (eight results)

The general mean is therefore 79.31.

The values given in the most recent standard tables of atomic weights are as follows:

German Chemical Society, Ber. **31**, 2761 (1898)	79.1
F. W. Clarke (J. Am. Chem. Soc. **22**, 70 (1900)	79.2
Richards (table for 1899, quoted by Clarke)	79.2

2. Boiling-point

Carnelley and Williams (1879) found a value lying between 676° and 683°. Their method of determining the temperatures was by using substances of high melting-point previously determined, and exposing them to the vapor of the boiling liquid.

Troost (1882) found the boiling-point to be at about 665° under a pressure of 760 mm. The temperature was measured with a form of air thermometer.

3. Vapor-density

Sainte-Claire Deville and Troost (1863), in their researches on vapor-density at high temperatures, determined that of selenium at 1420° and found it to be 5.68, corresponding to a molecular weight of 164.0. The values for the molecular weight at lower temperatures are:

	Mol wt
At 1040°	184
At 860°	222

4. Spectrum

In 1863 Werther published a note on the similarity between the spectra of selenium and lead. Ditte (1871) made a comparative study of the spectra of sulphur, selenium, and tellurium. He found well marked yellowish-green lines in the selenium spectrum toward the E line, and also two brilliant blue bands near to and to the left of the G line.

The work of Salet as well as that of Plücker and Hittorf is summarized in the report of a special committee of the British Association for the Advancement of Science (1884). The tables there given are too long to be quoted here.

5. Absorption spectrum

Gernez (1872) records that the vapor of selenium absorbs the rays of the spectrum up to about the C line; but at higher temperatures there is extinction in the blue and violet.

6. Capillarity constant

Quincke (1868) determined the capillarity constant of selenium by the method of drops, and found

$$\alpha = 7.180 \text{ mg for } 2r = 1 \text{ mm.}$$

VII. CONCLUSION

In conclusion, I desire to express my sincerest thanks to Professor W. D. Bancroft, in whose laboratory this work was carried on; I am indebted to him not only for suggesting the subject of the investigation to me, but also for his continued interest and timely suggestions while it has been in progress.

Cornell University, May, 1900.

AN EXPOSITION OF THE ENTROPY THEORY

BY J. E. TREVOR

Introduction

During recent years it has become more and more generally understood that the formulation of reversible additions of heat to a body or system of bodies, as the product of the thermodynamic temperature into the differential of the entropy of the system, is in all respects analogous to the formulation of the potential theory in mechanics. Mach's[1] remarkably intelligent views of the matter have done much — very much — to educate current opinion concerning it. But a logical exposition of the subject, in detail and with due consideration of every step of the development, is as yet lacking; to supply it is the object of the present paper. I am strongly of the opinion that an exposition of this sort is essential to a sound understanding of the general principles of thermodynamics; and that such an exposition should be the most prominent feature of every introductory course of instruction in the subject. The difficulties rapidly disappear when the argument that is actually at the bottom of the theory is consistently followed through.

In a former note,[2] I attacked the problem; but I failed at that time to establish in a wholly general way the existence either of a uniquely determinate thermal potential, or of the entropy function of any given thermodynamic system. In the present paper these imperfections are removed. The correct statement of the theory, as I understand it, is as follows.

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[1] See Mach: Erhaltung der Arbeit, Prag (1872); Mechanik (1883)-(1897); Sitzber. Akad. Wiss. Wien, 51, 1589 (Dec., 1892); Pop. Sci. Lecs, Chicago and Leipzig (1894)-(1898); Die Principien der Wärmelehre, Leipzig, (1896)-(1900).

[2] Jour. Phys. Chem. 3, 339 (1899).

The level theory

To begin with, we may define the thermodynamic changes of a body or system of bodies, in general of a 'system', as those which may be described in terms of the additions, positive and negative, of work and heat to the changing system. We know these additions of work and of heat, in any reversible thermodynamic operation, to depend upon the path pursued between the end states of the system; wherefore the infinitesimal additions $d'W$ and $d'Q$ must be represented as functions of the state-variables $x_1, x_2, \ldots$ of the system, and of their differentials, in the forms

$$d'W = Y_1 dx_1 + Y_2 dx_2 + \cdots$$
$$d'Q = X_1 dx_1 + X_2 dx_2 + \cdots,$$

where the dynamic and thermal coefficients Y and X are functions of the state-variables. The second members of these equations not being total differentials, we adopt for the quantities of work and heat taken up in any given finite change between the end states *a* and *b* the notation

$$W_{ab} = \int_a^b \sum Y dx$$

$$Q_{ab} = \int_a^b \sum X dx.$$

Considering, now, any cycle of thermodynamic operations, reversible or otherwise, we reach the familiar conclusion that the algebraic sum of the work and heat assumed by the system during the cycle must vanish, else uncompensated physical changes would result, in conflict with the principle of relativity; whence follows that in any thermodynamic change of state the algebraic sum of the work and heat assumed is equal to the change of a function $E(x_1, x_2, \ldots)$, the 'energy,' of the state-variables of the system; that

$$W_{ab} + Q_{ab} = E_b - E_a,$$

and, correspondingly,

$$dE = d'W + d'Q. \tag{1}$$

In order to utilize this equation (1), to obtain relations between the state-variables, it is necessary to express $d'W$ and $d'Q$ in terms of the state-variables, or functions of them, and their changes. We can do this immediately for the work-term, which is in any case the product of the acting force into the change of space through which the force acts; but we must seek a similar formulation of the heat term. We have, indeed, the relation

$$d'Q = X_1 dx_1 + X_2 dx_2 + \dots ;$$

but it does not serve our purpose, since we know nothing in general about the forms of the functions X.

The problem is solved by formulating the heat differential $d'Q$ after the pattern adopted in a similar case of very simple character. Just as work can be stored as heat and regained as work in reversible thermodynamic operations, so can work be stored in changing the position of a body in a field of gravity, and be regained in the reverse operation. In the former case, the heat developed is a store of thermal work-equivalents; in the latter the body in its new position represents — carries — a store of position work-equivalents.

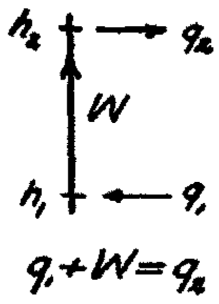

Fig. 1

Suppose, for example, that a body whose weight is w is to be raised by means of a relatively weightless elevator, a cord, in a constant field of gravity between the heights h_1 and h_2. The work-equivalents added to the working system, to the elevator, are $q_1 = h_1 w$, while those $q_2 = h_2 w$ are given out at the higher level. Denoting the expended work by W, the operation is represented by the diagram. Here, because of the energy law, we have $q_1 + W = q_2$. If the weight of the elevator be not negligible with reference to that of its load, an excess of work will be requisite for the transport of the load; wherefore, to keep the situation as simple as before, the elevator must be returned to its initial position at the close of the operation. The working system will then have traversed a cyclical operation of two constant-level and two adiabatic ($d'q = 0$) paths — a Carnot cycle. And the operation must be wholly reversible, in order that no work shall be wasted in overcoming friction, viscosity of the surrounding medium, or the like. It is obvious that in the change of the working system between two states *a* and *b* of level and load, the quantities W_{ab} and q_{ab} are not equal to changes of functions of the state-variables. Now, in any constant-level addition of work-equivalents to the system, we have

$$q_{ab} = h(w_b - w_a),$$

where w_a and w_b are the weights of the system before and after the addition. The addition may be construed as an addition of the weight

$$\frac{q_{ab}}{h} = w_b - w_a\,;$$

or, for an infinitesimal change,

$$\frac{d'q}{h} = dw.$$

In the equation

$$d'q = hdw$$

we have a formulation of the work-equivalents differential $d'q$ in terms of the state-variables and their changes.

If, for any changes of the state of level and load of our working system, we should know the values of the additions of work and of work-equivalents, but not those of the changes of level and of weight of the system, we could find the latter by:

(*a*) Measuring changes of level by the number of equal-work Carnot cycles in any given *series* of cycles between the two levels;

(*b*) Measuring changes of weight by the total work-value of the unit-height Carnot cycles that correspond to the actual additions of work-equivalents.

By a *series* of Carnot cycles is meant a series in which, at any level, the same quantity of work-equivalents (that is to say, the same weight) is given out and taken up. The unit difference of level would be fixed by assigning a fixed number of cycles to the change between two given levels. We should then have, even for additions at continuously varying levels, the changes of weight given as before by

$$\frac{d'q}{h} = dw;$$

or, over a finite path between the states a and b,

$$w_b - w_a = \int_a^b \frac{d'q}{h}.$$

It remains, now, to examine whether reversible additions of thermal work-equivalents, of heat, can be formulated in the way adopted here to yield the result

$$d'q = hdw.$$

The thermal potential

The thermal level, the work-level of a store of heat, the analogue of the level (height) of a body carrying a store of position work-equivalents, is the temperature—measured on any arbitrary temperature scale. For, in thermodynamic Carnot cycles, work may always be expended to change the temperature of a store of heat, or a difference of temperature may be utilized for the reversible production of work. In adiabatic thermodynamic changes, expenditure of work changes the temperature of a working system; but changes of other state-variables are necessarily involved also, for which reason it becomes necessary here, as in the preceding case, to consider the reversible mutual transformations of work and heat that are effected in the action of Carnot cycles. The result of the action of such a cycle is that the working system assumes a quantity of heat Q_1 at the lower thermal level τ_1, absorbs a quantity of work w, and develops the sum of the two as heat Q_2 at the higher level τ_2. This result may be represented diagrammatically in exactly the same way as before. The operations in question must be reversible, for the reason given in the consideration of the storing of work as position work-equivalents: to the end that no work shall be wasted in effecting irrelevant outstanding changes. This reversibility will be tacitly assumed through-

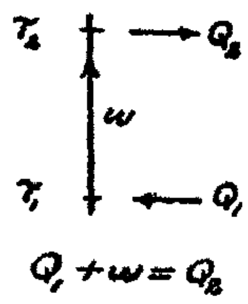

Fig. 2

out the following discussion. It is now to be examined whether the following definition gives a unique determination of differences of thermal level, or, as we shall better say, of thermal potential.

DEFINITION I. — *The difference of thermal potential corresponding to the difference of two given temperatures shall be measured by the number of equal-work Carnot cycles in any series between the two temperatures.*

By a *series* of Carnot cycles is to be understood, as before, successive cycles in which the same quantity of work-equivalents, here of heat, is developed and absorbed at any same temperature. To prove that this measure of thermal potentials is independent of the cycles and of the working system, we must have recourse to another physical principle, the so-called 'principle of the excluded perpetual motion of the second kind.' This principle asserts that: *A store of heat at constant temperature cannot be converted into work, without outstanding compensation.* Were this theorem not true, one could, for example, construct a motor to develop work at the expense of the constant-temperature heat of the atmosphere or of the sea.

An immediate consequence of this principle is the theorem: *The work-value of a thermodynamic Carnot cycle working between two given temperatures is independent of the cycle and of the working system, when a given quantity of heat is assumed at one of the temperatures.* For, suppose two Carnot cycles, working between the temperatures τ_1 and τ_2, to assume the quantity of heat Q_1 at τ_1, and to have the different work-values w and w'. Reversing one of them, the action of the two is represented by the double diagram

Fig. 3

Assuming $w' > w$, we have $Q'_2 > Q_2$, and

$$Q'_2 - Q_1 = w'$$
$$Q_2 - Q_1 = w,$$

whence, by subtraction,

$$Q'_2 - Q_2 = w' - w;$$

i. e., we find a production of the positive finite work $w' - w$ at the expense of the constant-temperature heat $Q'_2 - Q_2$, a perpetual motion of the second kind. Excluding this inadmissible result, we have

$$w' = w,$$

which was to be proved.

An extension of this theorem is the further one, that: *Working between two given temperatures, a thermodynamic Carnot cycle with a k-fold assumption of heat at either temperature has a k-fold work-value.* To see this, consider two consecutive cycles, as represented schematically in the figure.

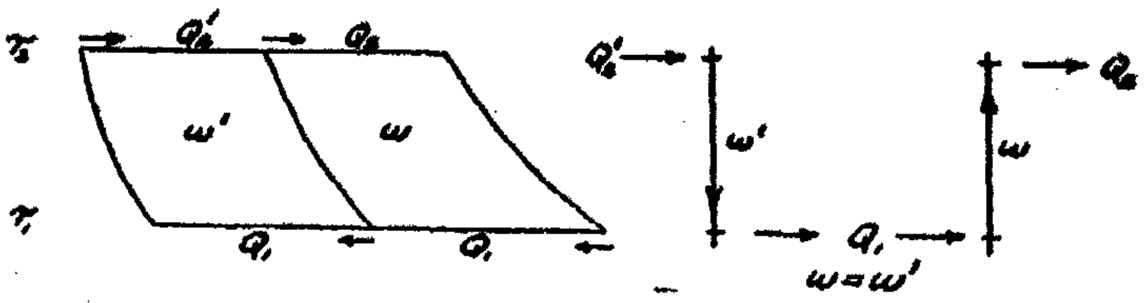

Fig. 4

Since the two cycles involve the assumption of the same quantity of heat at τ_1, they have the same work-value. Further, the two are equivalent in effect to one cycle with the assumption of $2Q_1$ at τ_1; and, similarly, k consecutive cycles are equivalent to one cycle with k-fold Q_1 and w. The value of Q_1 being arbitrary, our theorem follows.

This theorem serves to prove that our proposed measure of differences of thermal potential is independent of the cycle, and of the working system, used to effect it. For, suppose a series of equal-work thermodynamic Carnot cycles, the same number of cycles being taken between the same end temperatures, to connect at intervening temperatures different from those met by another series with the same or with a different working system. Consider the first three levels of the latter series, — as represented by the right-hand part of the accompanying diagram.

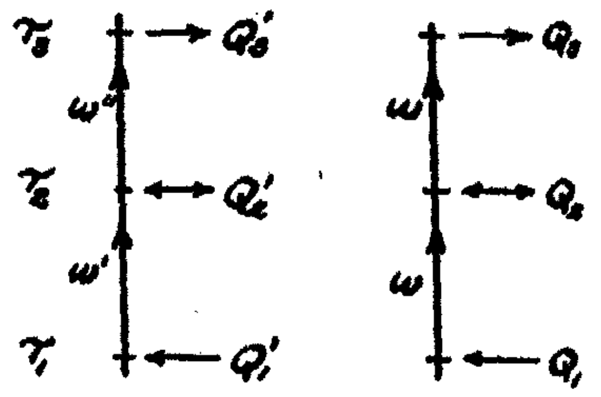

Fig. 5

Since the second cycle of the other series is supposed to connect at another temperature than τ_3, the cycle between τ_2 and τ_3 must have a work-value w'' different from w'. We have

$$Q'_1 = k.Q_1;$$

and, correspondingly, by the theorem just derived,

$$w' = k.w$$

$$w' + w'' = k.2w;$$

whence, doubling the first equation and subtracting,

$$w'' - w' = 0.$$

That is to say, the two series of equal-work Carnot cycles must connect at the same intervening temperatures; else a perpetual motion of the second kind would be realizable.

This result, that any difference $\theta_2 - \theta_1$ of thermal potential, as defined, is uniquely determined by the corresponding difference of temperature $\tau_2 - \tau_1$, shows that the thermal potential θ is a single-valued function of the temperature τ — measured on any arbitrary scale; that

$$\theta = \theta(\tau).$$

The unit difference of thermal potential is, of course, to be fixed by assigning a fixed number of cycles to the change between two given temperatures.

Now the thermodynamic Carnot cycles differ in one important respect from the mechanical ones whose formulation we are using as a model. When a body is raised in a field of gravity, the work thereby expended is stored as position work-equivalents; and, in the same way, the work expended in a thermodynamic Carnot cycle is stored as thermal work-equivalents — as heat. Our scheme of diagrammatic representation indicates this plainly:

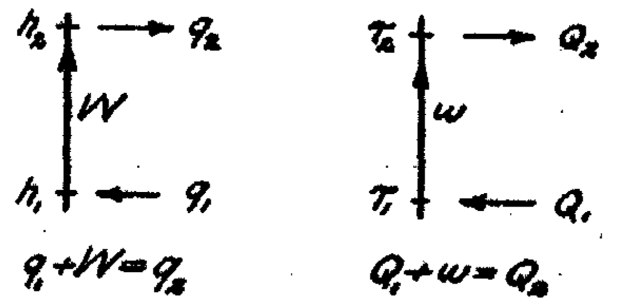

Fig. 6

In the first case, however, the work-measure of the quantity of work-equivalents added to the working system at any level is given solely by the work of the series of Carnot cycles requisite to store it there, starting from any arbitrarily chosen zero level; while in the second case the work-measure of the quantity of heat added at any thermal level is *codetermined* by the work-measure of the effect brought about, i. e. by the quantity of work requisite to develop the heat — through friction, for example.

Consider, now, a series of one-degree[1] unit-work thermodynamic Carnot cycles, as represented diagrammatically in Fig. 7. Unit work is stored as heat in each cycle; at the potential θ

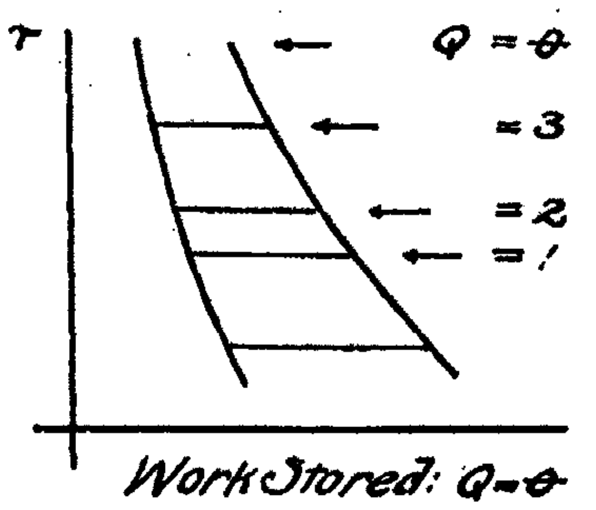

Fig. 7

the quantity $Q = \theta$ is stored. But the quantity of heat actually taken up at any potential has an independent work-measure, and

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[1] I. e., one unit of thermal potential.

therefore determines the value of that potential, and, correspondingly, of all the others. That is to say, the zero thermal potential $\theta = 0$ cannot be arbitrarily chosen. It appears, then, that, theoretically, the determination of the numerical value of the thermal potential corresponding to a given temperature is identical with the determination of the work-measure of the heat that is added at that temperature to any one-degree unit-work Carnot cycle. And it is plain that the scale of thermal potentials has a real physical meaning only in so far as it refers to the range of accessible temperatures. If, indeed, the zero of the scale of thermal potentials should be reached, and it should be found physically possible to pass to yet lower temperatures, this circumstance would not invalidate the formulation of thermodynamic theory: it would show merely that, through the range of accessible temperatures below that corresponding to the zero thermal potential, no differences of temperature could be utilized for the production of work.

The entropy

Having established our definition of the scale of heat-levels, or thermal potentials, we must consider the possibility of determining the changes of heat-weight of a thermodynamic system. Pursuing the analogy with the mechanical case formulated at the outset, we are led to the following definition.

DEFINITION II.— *The changes of the heat-weight of a system shall be measured by the total work-value of the one-degree Carnot cycles that correspond to the system's simultaneous absorptions of heat.*

The proof that this measure is independent of the cycle follows, as in the case of our Definition I., from the principle of the excluded perpetual motion of the second kind. From this principle follows, first: *When a given working system passes isothermally and reversibly from one state to another, the work-value of any corresponding one-degree Carnot cycle is independent of the isothermal path pursued between the two states.* Let I and I′, in the accompanying figure, represent any two isother-

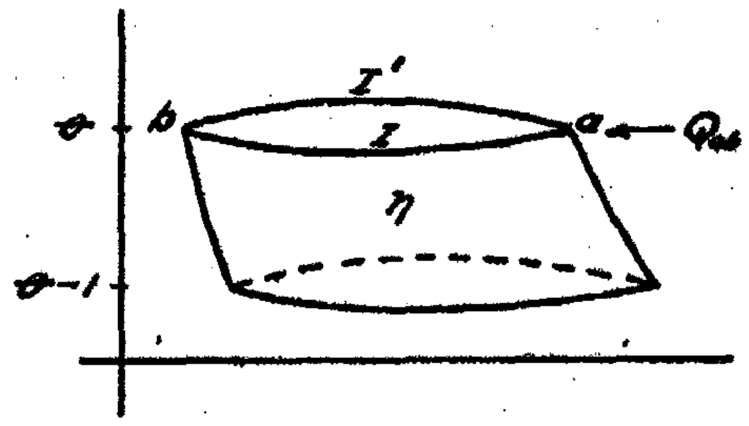

Fig. 8

mal paths of the system between the states *a* and *b*. The change of energy is the same along each path :

$$
\begin{aligned}
E_b - E_a &= W_{ab} + Q_{ab} \\
&= W'_{ab} + Q'_{ab}.
\end{aligned}
$$

Further, the quantities of work W_{ab} and W'_{ab} are equal, else a cycle forward on one path and back on the other would yield a perpetual motion of the second kind ; whence follows that

$$Q_{ab} = Q'_{ab} ;$$

and therefore, by a previous theorem, that the work-value η of the one-degree Carnot cycle is independent of the isothermal path, — which is the theorem that was to be proved.

An extension of this result is that: *The algebraic sum of the work-values of all the one-degree Carnot cycles corresponding to the heat additions of a reversible path between two given states of a working system is independent of the path.* In the accompanying Fig. 9, let the heavy line *ab* represent a given re-

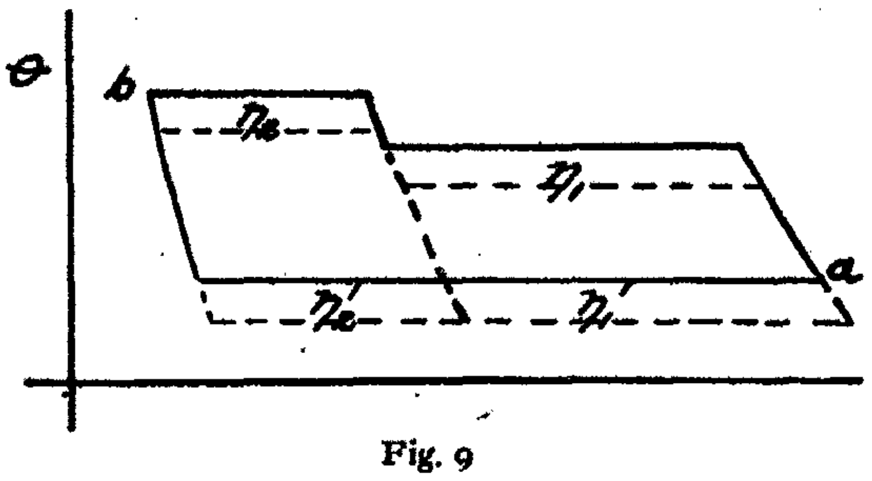

Fig. 9

versible path between the states *a* and *b*. The up and down lines represent adiabatic paths. The one-degree Carnot cycles that correspond to the heat additions of the path *ab* are marked with their work-values η_1 and η_2. These work-values are equal, respectively, to the work-values η'_1 and η'_2 of the one-degree Carnot cycles, of the same series, that correspond to the heat additions of an isothermal path between adiabatic paths passing through the end states. For, since Carnot cycles of equal work-values in any same series correspond to equal changes of thermal potential, it follows that any two one-degree Carnot cycles in the same series have the same work-value. It is plain that a similar conclusion may be drawn in regard to *any* reversible path between *a* and *b*, if we assume that any infinitesimal addition of heat may be regarded as isothermal; so the sum $\Sigma'\eta$ for any such path is equal to the sum $\Sigma''\eta$ for any other; i. e.

$$\sum \eta = \text{const.}$$

This being the case, the sum $\Sigma\eta$ is equal to the change $\eta_b - \eta_a$ of a function

$$\eta = \eta(x_1, x_2, \ldots) \qquad (3)$$

of the state-variables of the working system.

This function η, the heat-weight of the working system, is known as the 'entropy' of the system. Its change is the quantity-coordinate of the corresponding additions of heat: it is the 'thermal quantity-coordinate' that corresponds to the 'thermal potential' $\theta(\tau)$. We have, thus, as wholly analogous quantities:

Position work-equivalents;	Thermal work-equivalents (heat);
Height;	Thermal potential;
Weight of a system;	Entropy of a system.

The heat added isothermally to any thermodynamic working system along a path *ab*, being equal to the work stored in the corresponding series of Carnot cycles, is

$$Q_{ab} = \theta(\eta_b - \eta_a).$$

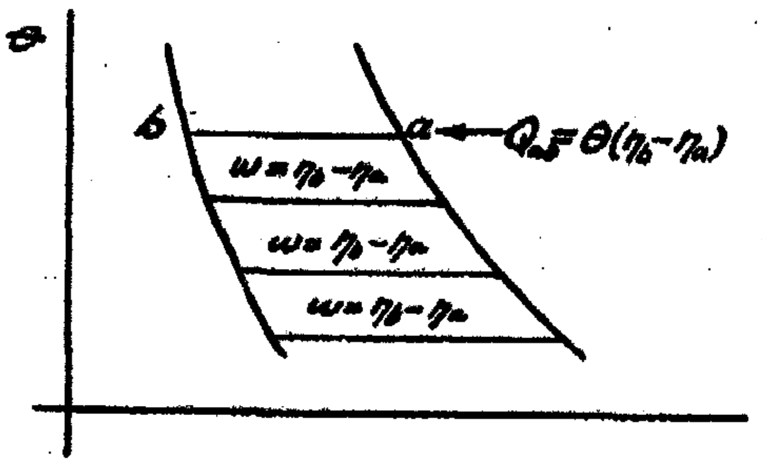

Fig. 10

Since the quantity η is a function of the state-variables of the system, this addition can be construed as an addition of the amount of thermal quantity-coordinate

$$\frac{Q_{ab}}{\theta} = \eta_b - \eta_a.$$

And, since all infinitesimal additions of heat are regarded as isothermal, we have, for the element of any reversible path,

$$\frac{d'Q}{\theta} = d\eta\,;$$

and, accordingly, the desired formulation of the addition of thermal work-equivalents as

$$d'Q = \theta d\eta, \tag{4}$$

in terms of the functions

$$\theta(\tau)$$
$$\eta(x_1, x_2, \ldots)$$

of the state-variables of the system. The τ is either one of the state-variables, or a function of the state-variables.

In the formulation

$$\frac{d'Q}{\theta} = d\eta,$$

the thermal potential $\theta(\tau)$ appears as an integrating divisor of the heat-differential

$$X_1 dx_1 + X_2 dx_2 + \ldots.$$

It might be defined, with reference to this expression, as the integrating divisor that is a function of the temperature alone; for when an integrating divisor is a function of but one of the variables it is unique,[1] a mathematical theorem whose first recognition arose from the thermodynamic considerations here presented.

It may be stated, finally, that with the thermal potential function $\theta(\tau)$ once determined, the determination of the changes of entropy of a system of bodies becomes merely an evaluation of the indicated integral in the equation

$$\eta_b - \eta_a = \int_a^b \frac{d'Q}{\theta}.$$

The entropy being a function of the state-variables, this equation becomes, for any cyclical reversible thermodynamic path,

$$\int \frac{d'Q}{\theta} = 0.$$

The energy equation

The object of this thermodynamic theory, as stated at the outset, is so to formulate the heat differential $d'Q$ that the energy equation (1),

$$dE = d'W + d'Q,$$

can be utilized to furnish relations between the state-variables of thermodynamic systems. This having been accomplished, in equation (4),

$$d'Q = \theta d\eta,$$

we have, as the general formulation of purely thermodynamic operations,

$$dE = d'W + \theta d\eta. \qquad (5)$$

The further formulation of $d'W$, as the product of the acting force into the corresponding change of space, offers no difficulty.

This rigorous development of the entropy theory brings out the exact character of the resulting formulation; and it makes

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[1] Paul Saurel. Jour. Phys. Chem. 2, 116 (1898).

clear, as Mach points out, just what the guiding ideas have been in the actual historical development of the theory. To most people, too, this sort of derivation is likely to appeal more strongly than one which involves assumption of the properties of 'ideal gases,' of substances which exist only in the imagination.

Cornell University,
April, 1900.

ENTROPY AND HEAT-CAPACITY

BY J. E. TREVOR

1. **Adiabatic paths.** — The question may be asked: What is the relation between the entropy of a system of bodies and the heat-capacity of the system with respect to any reversible thermodynamic path? For the particular case of adiabatic paths, the entropy η may be regarded as a sort of heat-capacity, in the following way. From the equation

$$d(\theta\eta) = \theta d\eta + \eta d\theta \qquad (1)$$

for the differential $d(\theta\eta)$ of the store of heat — of Helmholtz's 'bound energy' — of a system, we find

$$\eta = \left(\frac{\partial(\theta\eta)}{\partial\theta}\right)_{\eta}; \qquad (2)$$

which equation interprets the entropy as the increase of the store of heat, per degree, during adiabatic change, — as the heat-capacity for heat produced from adiabatic work.

This conception resembles that of Helmholtz,[1] that "The entropy appears as the heat-capacity for heat produced at the expense of the free energy during adiabatic change." Helmholtz's idea is deduced from his formulation of the energy as the sum of the free and bound energies of the system:

$$E = F - \theta\eta$$

$$\begin{cases} dF = d'W - \eta d\theta \\ d(\theta\eta) = \theta d\eta + \eta d\theta, \end{cases}$$

from which last equation the term $\theta d\eta$ disappears for adiabatic changes. But the matter is unnecessarily complicated by thus

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[1] Helmholtz. Ueber die Thermodynamik der chemischen Prozessen. Ges. Abh. 2, 958 (1882).

treating the term $\eta d\theta$ as supplied by the free energy; it is far more rational to regard it as the work that is expended in increasing the store of heat $\theta\eta$ of the system, while the remainder $(d'W - \eta d\theta)$ of the work is the contribution from without to the store of free energy.

2. The general case. — To formulate generally the relation between the entropy and the heat-capacity of a thermodynamic system, we proceed essentially as before. In (1) we have

$$d(\theta\eta) = \theta d\eta + \eta d\theta,$$

or, per degree,

$$\begin{aligned}\frac{d(\theta\eta)}{d\theta} &= \frac{d'Q}{d\theta} + \eta \\ &= C + \eta, \qquad (3)\end{aligned}$$

setting C for the heat-capacity $d'Q/d\theta$. Equation (3) is, of course, subject to the conditions which determine the path.

This equation (3) states simply that, on any path, the heat $d'Q/d\theta$ added per degree, and the work $\eta d\theta/d\theta$ stored per degree as heat, together give the total increase per degree of the store of heat.[1] Otherwise worded: a system's entropy, plus its heat-capacity with reference to any reversible path, is equal to the change per degree, on the same path, of the system's store of heat $\theta\eta$.

3. Further illustration. — Further to illustrate the general relation

$$C + \eta = \frac{d(\theta\eta)}{d\theta},$$

let the line ab in the accompanying figure represent any reversible path between two states, of any thermodynamic system of bodies, having a temperature-difference of one degree. The ordinates of the diagram represent the thermal potentials, — the 'absolute temperatures', — while the abscissas give a general representation of the remaining state-variables.

Drawing adiabatic lines through a and b, and an adiabatic

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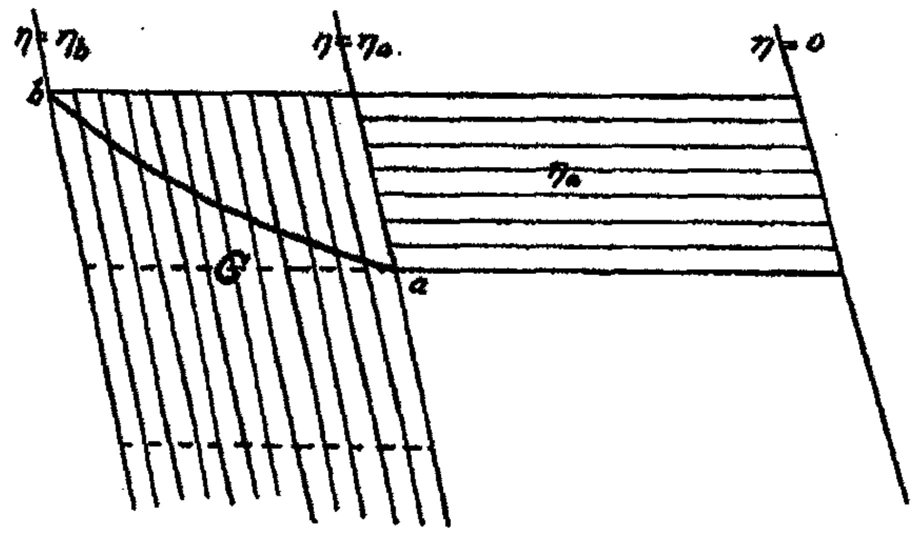
[1] I. e., the heat-capacity C is the heat added per degree, and the entropy η is the work stored, per degree, as heat.



line through the zero state of reference, we see that the entropy η_a at the state *a* is the work-value of the horizontally shaded one-degree Carnot cycle. For the changes of the entropy of a thermodynamic system are defined as the total work-values of the one-degree Carnot cycles that correspond to the heat-additions of any reversible path between the end-states of the system.

Further, the heat-capacity C of the system is the work-value of the vertically shaded Carnot cycle, regarded as extending to $\theta = 0$. For

$$\mathrm{C} = \frac{\theta d\eta}{d\theta}$$
$$= \theta(\eta_b - \eta_a),^1$$

and $(\eta_b - \eta_a)$ is the work-value of a one-degree Carnot cycle between the adiabatics $\eta = \eta_b$ and $\eta = \eta_a$.

Again, the quantity

$$\frac{d(\theta\eta)}{d\theta}$$

is the sum of the work-values of the two shaded Carnot cycles. For

$$\frac{d(\theta\eta)}{d\theta} = (\theta + 1)\eta_b - \theta\eta_a\,;^1$$

and $(\theta + 1)\eta_b$ is the work-value of the entire series of one-degree Carnot cycles between the adiabatics $\eta = \eta_b$ and $\eta = 0$, and from

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[1] Very approximately. We assume that $d\eta/d\theta = \text{const.}$, for the given path and through the temperature interval of one degree.

$\theta = 0$ to $\theta = \theta + 1$; while $\theta\eta_a$ is that of the series between $\eta = \eta_a$ and $\eta = 0$, and from $\theta = 0$ to $\theta = \theta$.

Thus the quantity

$$\frac{d(\theta\eta)}{d\theta}$$

appears as the sum of the quantities η_a and C, which is the relation whose physical significance was to be made clear.

Cornell University,
February, 1900.

THE RELATION OF THE TASTE OF ACID SALTS TO THEIR DEGREE OF DISSOCIATION, II

BY LOUIS KAHLENBERG

In a previous article[1] on this subject, it was shown that the sour taste of solutions of acid sodium salts is much more intense than it ought to be according to the assumption that sourness is caused by hydrogen ions only. Recently Richards[2] has attempted to explain this fact, and also the one that weak acids in general have a much stronger sour taste than they ought to have, according to their degree of electrolytic dissociation, by assuming that the act of tasting removes hydrogen ions and thus induces the formation of more, — the newly ionized hydrogen being again removed, and so on; thus, as the result of a cumulative effect, as it were, a far greater change may be caused on the tongue surface than corresponds to the concentration of the hydrogen ions in the solution in question. This conclusion, he states, is wholly in accord with the facts. At first sight this explanation seems to be a plausible way out of the difficulty; nevertheless, it is fallacious as the following considerations will show.

Richards states that there are two ways in which an acid may act in causing sour taste: — either catalytically or else by direct combination — he decides in favor of the latter. This is the view that has commonly been held heretofore and which I also accept. But it must be acknowledged that Richards's reason as to why the action may not be catalytic, namely, that on this assumption the sour taste of acid salts and weak acids can

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[1] Jour. Phys. Chem. 4, 33 (1900).
[2] Ibid. 4, 207 (1900).

not be accounted for by means of the dissociation theory, is a very poor one. Richards does not give his reason in the words here used, but his statements virtually amount to the same thing. In order not to do him any injustice, I shall quote the passage in which he gives the reason just referred to, which will enable the reader to judge for himself.

"If the action is catalytic, the change in the concentration of the hydrogen ion in the neighborhood of the nerve terminal during the reaction cannot be large, for any acid existing in the tongue surface must be exceedingly weak. Hence taste should be a fairly accurate indicator of the concentration of the hydrogen ion. This assumption leads us to a result in opposition to the facts; in order to maintain it, one must make the unlikely extra assumption that a complex body is capable of producing the simple effect caused by ionized hydrogen."

The most dilute solution of hydrochloric acid that can still be tasted is somewhat stronger than *n*/1000 according to Richards. My own determinations place the limit at about *n*/800. A solution of hydrochloric acid, say, for example, *n*/1500 is therefore without sour taste. One can take such a solution into the mouth, hold it there for some time, moving the tongue about and rubbing it against the palate without experiencing sour taste. One can even eject the mouthful, take a fresh mouthful, retain it for a while and repeat this operation indefinitely without experiencing sour taste. Now, granting that hydrogen ions are used up in the tongue surface, we surely, by the process just mentioned, repeatedly bring a fresh lot of them into contact with the tongue (to be sure never in a greater concentration than *n*/1500) and thus offer a good opportunity for a cumulative effect to take place. The *n*/1500 solution after being held in the mouth is by no means devoid of acidity (i. e., of hydrogen ions, if we accept the dissociation theory) as tests other than taste readily show. It is clearly not possible to make a *n*/1500 solution of hydrochloric acid give one the sensation of sourness, no matter how good a chance for cumulative effect is given it; although the *n*/1500 would only have to double its effect in order to cause sour taste to be experienced. These experiments show (speaking in the language of the theory of the electrolytic dissociation) that a *minimum initial concentration of hydrogen ions must be present in the solution in order that sour taste may be experienced*, this concentration being say, slightly greater than *n*/1000. The initial concentration of hydrogen ions, for example, in a solution of acid sodium malate containing 1 g mol in 128 liters is *n*/17800 according to W. A. Smith's measurements; yet this solution has a pronounced sour taste, which is equal to at least that of a *n*/400 hydrochloric acid solution. This sodium acid malate solution would on Richards's assumption have increased its sour taste by cumulative effect over forty times. Similar equally striking results might here be detailed in case of other acid salts. Now since a *n*/1500 solution of hydrogen ions can not (even when the hydrogen ions used up are continually renewed from a fresh solution of the same strength) by cumulative effect increase its action on the tongue to that of an *n*/800 solution, how much less can a *n*/17800 solution increase its effect to that of a *n*/400 solution? I take it that no one would hold that the organs of taste are able to concentrate hydrogen ions from weak acids or acid salts[1] until their concentration becomes somewhat greater than *n*/1000, and so sufficient to cause the nerves to report sourness; yet this assumption is necessary in order to explain satisfactorily the phenomena in question on the basis of the theory of electrolytic dissociation. The action of the sense of taste may in a way be compared with that of an indicator that, at best, is sensitive for hydrogen ions to *n*/1000 only. Every indicator has its limit of sensitiveness, and its action depends (as the action of an acid on the tongue probably also does) upon chemical combination. The establishment of a chemical equilibrium thus always results. All this, it must be remembered, however, does not necessarily involve acceptance of the theory of electrolytic dissociation for an explanation.

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[1] According to Ostwald, Zeit. phys. Chem. 9, 553 (1892), hydrogen ions are supposed to form with considerable difficulty in case of solutions of acid salts.

From the foregoing, it is evident that the taste of weak organic acids and of acid salts can not be explained on the basis of the theory of electrolytic dissociation by assuming that sour taste is caused by hydrogen ions only; the further assumption that a larger complex may cause the same simple effect that the hydrogen ion does is absolutely necessary. As the latter assumption is unlikely, as Richards also admits, I wish here to repeat the statement I have previously[1] made that the explanation of the sour taste of solutions of acid salts from the standpoint of the theory of electrolytic dissociation is unsatisfactory. I ought perhaps not to neglect to say in this connection that Richards[2] states that I ascribe the sour taste of acid salts to the anion (for instance, HC_2O_4'); this is not correct, however, as I have simply pointed out that this explanation follows when the phenomena are viewed in the light of the dissociation theory, as the reader will see by reading the last paragraph of my previous article[3] on this subject. Indeed, in that paragraph I have sought to make clear how unlikely this assumption is.

The fact that the taste of acids can not be satisfactorily explained on the basis of the theory of electrolytic dissociation does not mean that the chemical explanation of taste must be dropped. Acids and acid salts all have the same sour taste, and clearly this fact must be due to that which these substances all have in common,—namely, the chemical reactiveness that they possess by virtue of the hydrogen they contain that is replaceable by a metal of a basic radical. The more readily this hydrogen is replaced under the experimental conditions obtaining, the more reactive the acids are, the more intense is their taste. This view is the older one, yet it is in harmony with the facts as known at present. While the theory of electrolytic dissociation is not able to cope with the phenomena under consideration, it must be borne in mind that it deserves credit for stimulating the recent researches on taste.

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[1] l. c. p. 37.
[2] l. c. p. 207.
[3] l. c. pp. 36–37.

It may not be superfluous to recall here the fact that all the solutions of the acid salts tasted are odorless, and that consequently in tasting them there can be no confusion of taste and smell.

In conclusion, I desire to add that the toxic effect of solutions of acid sodium salts on *Lupinus albus* has recently been investigated in this laboratory. The results obtained are such as the taste experiments would lead one to expect; the dissociation theory does not offer a satisfactory explanation of the facts. The results of the researches on the toxic action of acid salts on *Lupinus albus* are ready for publication and will appear shortly in the pages of this Journal.

Since this article was written A. A. Noyes[1] has also tried to explain the phenomena in question by assuming a cumulative effect. His explanation is practically the same as that of Richards, and like the latter's, is shown to be fallacious by the above considerations.

Laboratory of Physical Chemistry,
University of Wisconsin,
Madison, May 29, 1900.

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[1] Jour. Amer. Chem. Soc. 22, 73, (1900).

NEW BOOKS

An Outline of the Theory of Thermodynamics. *By Edgar Buckingham. 14 × 22 cm; xi + 205 pp. New York: The Macmillan Company, 1900. Price: cloth, $1.90.* — In the preface of this newest book on thermodynamic theory, the author states that its aim is to bridge the gap between the existing textbooks and the modern memoirs. It is intended for the beginning student, and "Is not a book of applications, but a brief outline of the theory, the applications having been selected solely with a view to their illustrative value." In rough outline, the topics successively taken up are: Introductory Concepts; the First Law of Thermodynamics; the Second Law; the Criteria of Equilibrium.

The introductory chapter on Thermometry is lucid and brief. Chap. II., on Calorimetry, is a rather elaborate analysis of the idea of quantity of heat; six elements of the idea being considered. The discussion, however, is restricted to heating and cooling phenomena; and it is not emphasized that a quantity of heat is a purely auxiliary quantity, a more or less convenient but wholly arbitrary mathematical fiction. The concluding introductory chapter, on Material Systems in Thermodynamics, makes clear what is meant by a thermodynamic system of bodies, and limits the discussion to systems that have equations of equilibrium. Here the author presents an enthusiastic definition of thermodynamics as: "The study of all the properties or qualities of material systems, and of all the forms of energy that they possess."

The next three chapters are on the First Law. First we have a simple discussion of the law, which is sufficiently comprehensive and clear to give a good idea of it; then, under the title The Principles of Thermochemistry, an exposition of the law of constant heat sums, and of the relation between heat of reaction and temperature; and, finally, under the heading Calorimetric Properties of Fluids, the idea of specific heat in general, and of the two principal specific heats in particular, a study of the specific heats of ideal gases, and an account of the theorem of Reech. Here follows, in Chap. VII., a recapitulation of the results attained thus far. This completes the first half of the book.

The second half begins with Chap. VIII., on the Second Law of Thermodynamics; which treats reversible processes, the Carnot cycle, and Carnot's theorem; develops the idea of absolute temperature and of entropy, from the properties of ideal gases; and formulates, in terms of v, θ, the changes of entropy of an ideal gas. In Chap. IX., General Equations, the two laws are combined to give the differential equation for the energy of a system; change of variables yields the differentials of the Gibbsian functions ψ, χ, ζ, and the 'four thermodynamic relations' are derived therefrom; the first derivatives of these functions are discussed; and Gibbs's 'fundamental equations' are defined. Chap. X., on Applications, gives an admirably clear and consistent account of the theory of the porous plug experiment: this is one of the best things in the book. The chapter is concluded by simple treatment of the elasticity of a solid, of the electromotive force of a reversible cell, of the Clapeyron-Clausius equation, and of the osmotic pressure.

With Chapter XI., the Conditions [criteria] of Thermodynamic Equilibrium are taken up. This is the one distinctly unhappy chapter of the book; for the author has failed to see that the matter rests wholly on the inductively reached integral principle of the spontaneous dissipation of work-availibility. He does not even present Carl Neumann's reasoning anent the formula,

$$(\int) \frac{dQ}{\theta} \overset{=}{<} 0,$$

that he gives. The usefulness of this chapter will consist in disturbing the reader, and thereby inciting him to study the question for himself. The chapter is extended by the following one, on Thermodynamic Potentials and Free Energy; in which the criterion of equilibrium is expressed with the aid of the functions ψ and ζ, and Helmholtz's free energy equation is derived. In the final chapter, on Applications, we have, mainly, a discussion of the p, θ-diagram for the equilibria about a one-component fusion triple-point; and a derivation of the phase rule for systems in which no chemical combination occurs. The book is provided with an index.

From the above detailed description, it will be seen that Prof. Buckingham's outline treatment of thermodynamics is fairly comprehensive. Opinions will differ as to what should be included in an introductory treatise; but it seems to the writer that it would have been to the advantage of the book to have included a reference to thermodynamic surfaces, giving at least some account of Gibbs's energy surface; a derivation of the phase rule, at least in outline, in which chemical relationships should be considered; and, possibly, some reference to the attempts at a thermodynamic theory of reaction velocities. But it is, of course, quite possible to consider these things as relatively minor matters, and beyond the scope of the book.

Now, in point of general theory, there are two ways in which a treatise on theoretical thermodynamics can be written: an approximative way and an exact way. One can derive the absolute temperature and the entropy function from the properties of an ideal gas; or one can arrive at these functions from fundamental physical postulates (see the paper on An Exposition of the Entropy Theory, in the present number). Our author has chosen the former method, presumably for pedagogical reasons. But the latter method is more in harmony with the spirit of comparative physics; for it parallelizes the thermodynamic temperature with other potentials, the entropy with other quantity-coordinates, and brings out the distinction between forces and potentials and between spaces and quantity-coordinates. Furthermore, it is rigorous, which the other method is not; and it lends itself more readily to the development of a well-rounded and coherent body of theory.

Following the approximative plan, our author has given us a good treatise.

It is brief, as it should be for the beginner, who needs his *aperçu* first and his details later; and it is clearly thought out and clearly written. It is certainly as satisfactory a student's text as we have.

The beginning student will doubtless be thankful that this book is developed as a physical argument, rather than as a symmetrical mathematical analysis of the general problem presented by a small number of inductively established postulates. But he should remember, if ever he is to gain a grasp of the subject, that eventually he *must* understand his thermodynamics as a logical system of mathematically developed theory. *J. E. Trevor*

J. D. van der Waals. Ein Lebensabriss. *By J. J. van Laar. 14 × 22 cm; pp. 51. Leipzig: Johann Ambrosius Barth, 1900. Price: paper, 1.60 marks.* — This is an appreciation of the work of van der Waals, by one of his better known pupils. It is a warm tribute, of admiration and affection, to the man's work and to his life. Van Laar gives a popular discussion of van der Waals's characteristic equation for fluids, and the equation for two-component fluids; and a similar treatment of the later work on the thermodynamic theory of capillarity, and on the constants of the characteristic equation. He ventures into a comparison of van der Waals's scientific method with that of Maxwell, contrasting it with a similar comparison of the styles of Lorenz and Helmholtz. A brief and very interesting biography, and a bibliography of van der Waals's more important papers, forty-two of them, complete the brochure. *J. E. Trevor*

Die kinetische Theorie der Gase. *By Oskar Emil Meyer. Second, revised edition. 16 × 24 cm; pp. xvi + 352, with an appendix of 128 pp. Breslau: Maruschke und Berendt, 1899. Price: paper, 12 marks.*

The Kinetic Theory of Gases. *By Dr. Oscar Emil Meyer. Translated from the second, revised, edition by Robert E. Baynes. 14 × 22 cm; pp. xvi + 472. New York: Longmans, Green and Co., 1899. Price: cloth, $4.00.* — The first edition of Oskar E. Meyer's introductory treatise on the kinetic theory of gases appeared in 1877, since which time the book has exerted an enormous influence in popularizing the theory. After having been long out of print, it now reappears, in a revised German translation, and, simultaneously, in an English translation by the well known thermodynamicist Robert E. Baynes. The German edition appeared in two parts, in 1895 and 1899. They may be bought separately if desired.

Meyer's book is written primarily for the experimentalist. It aims to give an introductory account of the kinetic theory of gases considered as a physical theory; and to do so without the use of any mathematical apparatus. But, for the sake of reference, a compact exposition of the elements of the mathematical theory is added in an appendix (of 112 pages in the English edition). Part I. of the work presents, successively, the bases of the theory, the laws of pressure, Maxwell's law of the distribution of velocities, van der Waals's theory of fluids and allied hypotheses, and a discussion of the ratios of specific heats. Part II. treats molecular free paths, and the related phenomena of viscosity, diffusion, and the conduction of heat; and concludes with considerations regarding the sizes, numbers, and speeds of the hypothetical molecules.

Mr. Baynes has furnished an admirable translation of the original text;

and, happily, has added an index. The popularity of the first edition of the book will doubtless be transferred in large measure to the second; for the work certainly supplies what many people desire, an easy means of gaining a rudimentary familiarity with the kinetic theory. *J. E. Trevor*

Die Fortschritte der Physik. *Dargestellt von der physikalischen Gesellschaft zu Berlin. Im Jahre 1898: III. Abtheilung: Kosmische Physik: redigirt von Richard Asmann; pp. xlii + 586. 16 × 23 cm. Price: paper, 22 marks. Braunschweig: F. Vieweg und Sohn, 1900.* — The third part of the fifty-fourth volume of the *Fortschritte der Physik* is now out. It considers the work that falls under the head of Cosmic Physics; and the treatment is under the subheads of Astrophysics, Meteorology, and Geophysics. This part completes the review for 1898, thus maintaining the prompt service that has done much in late years to increase the value of this very important publication.

J. E. Trevor

Kleiner Leitfaden der praktischen Physik. *By Friedrich Kohlrausch. 14 × 22 cm; pp. xix + 260. Leipzig: B. G. Teubner, 1900. Price: bound, 4 marks.* — The larger volume now contains a great deal which the beginner must omit, and we have here a smaller work which is intended chiefly for those who wish to take a course in experimental physics, but who do not intend to specialize in that subject. The book is as admirable as one would expect; but it must be admitted that there are dangers in making an elementary book from an advanced one merely by elimination. It certainly is not fair to an elementary student to write (p. 31) without a word of comment:

$$\sqrt{\frac{p+l}{p+r}} = 1 + \frac{l-r}{2p} .$$

The weak part of the large book was the unnecessarily scrappy way in which the proofs were outlined. This becomes a positive defect in the smaller book. It would have been more satisfactory also if the author had described the copper voltameter as it is used. *Wilder D. Bancroft*

Aufgaben aus der Chemie und der physikalischen Chemie. *Zum Gebrauch für die oberen Klassen höherer Schulen. By P. Bräuer. 15 × 22 cm; 69 pp. Leipzig: B. G. Teubner, 1900. Price: bound, 1.40 marks.* — The author has collected for use in the upper classes of German High Schools problems bearing on the orthodox field of the balancing of equations, mass analyses, and the Boyle-Gay-Lussac law; and in addition he presents exercises in the application of the laws of Dulong and Petit, Joule, Ohm, and Faraday, and of those relating to the dissociation of gases, osmotic pressure, and thermochemical change. The application of physical chemistry to elementary work is urgently needed; and the author deserves commendation for his efforts in this direction. The book would be more acceptable to the American college student if the explanation at the beginning of each section were made more complete.

H. R. Carveth

Leçons d'Électrotechnique générale. *Professées a l'École supérieure d'Électricité. By P. Janet. 17 × 25 cm; pp. ix + 614. Paris: Gauthier-Villars,* *1900.* —This textbook for electrotechnical students appears to be admirably fitted to its purpose. It can serve also as a very satisfactory work of general reference for those whose chief interests lie in more or less remote fields. The author has undertaken rather to present the general aspects of his subject than to give descriptions of existing types of electrical machinery. He points out that, in any study, it is necessary both to apprehend and to comprehend; that one apprehends the particular and comprehends the general. He has made his book especially interesting, because he has aimed to enable his readers to comprehend.

In what may be called the introductory part of the book, we find a simple and clear exposition of the general principles of mechanics, thermodynamics, electrostatics, magnetism, and induction, and a study of insulating, conducting, and magnetic materials. The remainder of the text is devoted to the detailed general theory of dynamos, electric motors, and transformers. Besides being well planned and well written, the book, in its beautiful and tastefull printing, is a credit to its publishers. *J. E. Trevor*

Mesures électriques. *Essais de laboratoire. By E. Vigueron and P. Letheule.* (*Encyclopédie scientifique des Aide-Mémoire.*) *12 × 19 cm; pp. 180. Paris: Gauthier-Villars. Price: paper, 2.5, boards, 3 francs.* — The general arrangement is shown by the table of contents: introduction; electrical units; reading electrometric instruments; general measuring instruments; galvanometers; electrodynamometers and watt-meters; electrometers; discussion of errors; potential differences; currents; resistances; capacities; coefficients of self-induction; tables. *Wilder D. Bancroft*

La Télégraphie sans Fils. *By André Broca. 12 × 19 cm; vii + 202 pp. Paris: Gauthier-Villars, 1899. Price: paper, 3.50 francs.* — In a small book, of less than two hundred pages of large type, M. Broca gives us an exposition of the theory of the propagation of electric waves. He begins with a brief account of ordinary telegraphy; then develops in simple language the salient features of the electromagnetic theory of light; and thus passes to an account of the vertical-wire transmitter and the coherer receiver now in use in wireless telegraphy. The little book is an admirable specimen of what essays in popular science should be. Simply written, sound, and compact, it presents what the intelligent general reader really needs to know; presents it in a correct and interesting way; and stops when the task is finished. *J. E. Trevor*

Traction Electrique. *Extrait des Leçons professées a l'Institut électrotechnique Montefiore. By Eric Gérard. 17 × 25 cm; pp. vi + 136. Paris: Gauthier-Villars, 1900. Price: paper, 3.50 francs.* — This book is an extract, by the publisher, from the author's *Leçons sur l'Electricité* originally delivered at the *Institut électrotechnique Montefiore.* It is intended for the use of those who are directly interested in electric traction, but who have not the time to make an extended and detailed study of applied electricity. The book is descriptive, and wholly practical in its aims. *J. E. Trevor*

Volumetric Analysis. *Specially adapted to the requirements of students entering for the advanced practical chemistry examinations of the science and* *art department; also the intermediate science and preliminary scientific examinations of the University of London. By John B. Coppock. 13 + 19 cm; pp. 92. (Whittaker and Co.); New York: The Macmillan Co., 1899. Price: cloth, 50 cents.* — It does not seem too much to ask that books in English on scientific subjects shall be written in good English, and that the subject matter should be treated scientifically. If it is necessary, for the benefit of some particular body of students, to regard volumetric analysis from the point of view of fifty years ago, why print the book, and above all, why put it in the way of the unsuspecting public? One would have thought the writing of a book like this impossible after the appearance of Ostwald's excellent little treatise, but in the present volume, the theory of indicators is not touched upon, and all that seems to have been culled from modern chemistry appears in the account of the oxidation of ferrous sulphate by potassium permanganate, where we find the following: "Arrhenius in his theory of solution points out that substances do not exist as such in solution, but are more or less broken up into parts; e.g., a dilute solution of sulphuric acid contains the parts H_2 and SO'_4, hence the oxygen can at once oxidize the H_2 to H_2O and the liberated SO_4 at once attach itself to the ferrous sulphate."

Such passages as this are necessarily rare, yet the following is worth quoting too, as well for its scientific truth as for its style: "In all branches of analysis it is the aim of the chemist to produce the liquid state in so far as he is engaged on investigating chemical change."

The material in the work is essentially what is to be found in any book on the subject and is in the main clearly treated; hence one's regrets in reading it are rather for what it might have been and is not, than for what it actually is.

A. P. Saunders

The Calculations of Analytical Chemistry. *By Edmund H. Miller. 15 × 23 cm; pp. viii + 183. New York: The Macmillan Company, 1900.* —The book is apparently, indeed almost expressly, designed to be put into the hands of students; but if the student who should attempt to use it were quite a beginner he would be puzzled by the immediate use of chemical symbols, and references to valence, etc., which are unaccompanied by any explanation; on the other hand, if he had had sufficent training to be clear in his mind regarding valence, it would scarcely be necessary to treat him to eight pages of text and three pages of examples on atomic weights and equivalents. In little ways like this the work lapses now and again from the methodical, but there is much good material in it, and in the hands of a discriminating teacher it would be a valuable aid in connection with analytical drill. The ground covered includes all the kinds of analytical calculations the student is likely to be called upon to make, and each chapter is fortified by a long list of problems for calculation. Some details might be improved upon. For instance in the chapter on specific gravities the omission of all mention of the floating method is a grave one; and it is scarcely happy to refer to lithium as a substance soluble in water.

On the whole the book is a useful one, though not likely to inspire enthusiasm. At the end are tables of densities, ratios, etc., revised from modern sources, and finally logarithms and antilogarithms to four places.

A. P. Saunders

Produits aromatiques artificiels et naturels. *By George F. Jaubert.* (*Encyclopédie scientifique des Aide-Mémoire.*) *12 × 19 cm; 168 pp. Paris: Gauthier-Villars. Price: paper, 2.50; boards, 3 francs.*—This is one of a series of monographs, each covering some special part of the field of organic chemistry. The subject is treated under the following heads: aromatic alcohols; aromatic acids; terpenes; camphors; terpenic alcohols, aldehydes, and acids. *Wilder D. Bancroft*

Les Parfums comestibles. *By George F. Jaubert.* (*Encyclopédie scientifique des Aide-Mémoire.*) *12 × 19 cm; pp. 187. Paris: Gauthier-Villars. Price: paper, 2.5; boards, 3 francs.*—The object of this volume is to give "as complete data as is possible in regard to the many essences which are coming into ever greater use in many important industries." *Wilder D. Bancroft*

Annuaire de l'Observatoire Municipal de Paris, *dit Observatoire de Montsouris, pour l'année 1900; Météorologie, Chimie, Micrographie, Applications à l'Hygiène. 10 × 15 cm; pp. 578. Paris: Gauthier-Villars. Price: paper, 2 francs.*—In this *Annuaire* is published the work of the municipal observatory of Montsouris (Paris). The observations carried on are arranged under the heads: (a) Physics and Meteorology, (b) Chemistry, (c) Micrography.

J. E. Trevor

REVIEWS

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

General

The periodic system of Mendeleeff and the new constituents of the air. *A. Riccini. Gazz. chim. Ital.* 29, *I, 169 (1899).*—The point is made that the periodic system classifies elements according to the compounds that they can form and that, by definition, there can be no place in such a system for elements which form no compounds. *W. D. B.*

Representation of the periodic system of the chemical elements. *K. Schirmeisen. Zeit phys. Chem.* 33, *223 (1900).*—The single periods are represented as circles, and the double periods as figures of eight. *W. D. B.*

Reply to Mr. E. Cohen. *K. Schaum. Zeit. phys. Chem.* 32, *150 (1900).*—Exception is taken, apparently rightly, to the rather surprising attack made on the author by Cohen. *W. D. B.*

On some methods of correcting and eliminating the errors of capillarity in areometers. *G. Guglielmo. Rend. Accad. Lincei,* (5) 8, *II, 341 (1899)*; 9, *I, 9, 33, 71 (1900).*—A discussion of the sources of error in areometers and a description of several modified forms. *W. D. B.*

One-Component Systems

Physical-chemical studies on tin, II. *E. Cohen. Zeit. phys. Chem.* 33, *57 (1900).*—Some tin vessels, which were dug up in England in 1897 and which had presumably been buried about 350 A. D., are shown to consist of gray tin. *W. D. B.*

On the boiling-points of the form $CH_3.(CH_2)_nR$. *E. Boggio-Lera. Gazz. chim. Ital.* 29, *I, 441 (1899).*—The boiling-points can be expressed with surprising accuracy by the formula

$$T = k \sqrt{M + C}.$$

Here M is the molecular weight, while *k* and C are arbitrary constants, varying from one homologous series to another. In the cases tabulated, *k* only fluctuates between 35 and 39. The formula does not apply to substances of the type CH_3R. *W. D. B.*

On a manostat. *A. Smits. Zeit. phys. Chem.* 33, *39* (*1900*). — The author has devised and described an apparatus with which he can keep the boiling-point constant to within ±0.002°, no matter what the barometer variations are. A rise of 2° in the temperature of the room causes a rise of boiling point of 0.001° in the case of water. *W. D. B.*

On corresponding states. *K. Meyer. Zeit. phys. Chem.* 32, *1* (*1900*). — The question arose whether the variations from the van der Waals law of corresponding states are due to errors in the critical constants and this was answered in the negative. It was thought that the law of corresponding states might hold if expressed in new units, the differences between the volumes, pressures, and temperatures at two corresponding states being taken as the units. The reason for supposing that this would give a different result from the ordinary method was that the minimum volume under infinite pressure should be taken into account, and also that the absolute temperature was not necessarily a satisfactory unit. A difficulty arose in selecting the two corresponding states from which to deduce the new units. The critical point was one of them; but there was no theoretical method of fixing another point that could be determined experimentally. The values were therefore obtained graphically by sliding the curves for two substances about until they coincided. It was found that the pressure units were the same for all substances, while the temperature and volume units varied. The law of corresponding states, as thus formulated, holds for twenty-five substances within the limits of the experimental error. As might have been expected, it does not hold for the alcohols or for acetic acid, and apparently not for water, though the experimental error is so large in this case as to make any conclusion of doubtful value. *W. D. B.*

The volume of the molecule. *C. M. Guldberg. Zeit. phys. Chem.* 32, *116* (*1900*). — From the compressibility, the author has calculated the molecular volumes of a number of substances at the absolute zero, and has tabulated these values. Isomeric substances give different values. *W. D. B.*

The vapor-density of bromin at high temperatures. *E. P. Perman and G. A. S. Atkinson. Zeit. phys. Chem.* 33, *215, 577* (*1900*). — The vapor-density of bromin is practically normal up to 750°. From this temperature it falls rapidly being only 75 at 1050°. *W. D. B.*

On the calibration of a glass tube and some compressibility coefficients. *G. A. Hulett. Zeit. phys. Chem.* 33, *237* (*1900*). — The author fills the tube to be calibrated with mercury and draws off equal volumes by means of a pipette. He has also determined the coefficients of expansion of water and of *p*-toluidin with respect to mercury. *W. D. B.*

Two-Component Systems

On the formation and change of mix-crystals of mercuric bromid and mercuric iodid. *W. Reinders. Zeit. phys. Chem.* 32, *494* (*1900*). — Mercuric bromid and iodid form a continuous series of mix-crystals with a minimum melting-point. The author has determined the compositions of the co-existing phases along the freezing-point curve and has also studied the change of inversion temperature with the change of composition. Crystals of pure mercuric iodid change reversibly from red to yellow at 127°; at 50° the red crystals contain 4.3 molecular percents of mercuric bromid, and the yellow crystals 15.5; at 0° the values are 8.6 for the red crystals and 83.0 for the yellow. The distribution ratio points to the same molecular weight for mercuric bromid in the two sets of crystals. *W. D. B.*

On melting-points of mixtures of optical antipodes. *M. Centnerzwer. Zeit. phys. Chem.* 29, *715* (*1899*). — The author has determined the freezing-point curves for about a dozen pairs of optical isomers. In most cases the existence of a compound as solid phase is clearly marked, but in a few instances, the measurements do not justify the conclusions drawn by the author.

W. D. B.

Miscellaneous cryoscopic observations. *K. Auwers. Zeit. phys. Chem.* 32, *39* (*1900*). — Cryoscopic studies on the behavior of substituted phenols and of nitroso compounds in naphthalene followed by an investigation of methyl oxalate and *p*-azoxyanisol as solvents. Methyl oxalate has a very slight polymerizing tendency. With *p*-azoxyanisol all sorts of freezing-point constants were obtained, a result which fills the author with surprise and dismay, although it is probably due to the solute dissolving in the 'liquid crystals'. *W. D. B.*

The freezing-point method in dilute solutions and the theory of solutions. *M. Wildermann. Zeit. phys. Chem.* 32, *288* (*1900*). — A further discussion in which it is pointed that the results of other experimenters agree more and more closely with those of the author as the other experimenters become more and more expert. *W. D. B.*

Studies on the theory of vapor-pressure. *R. Gahl. Zeit. phys. Chem.* 33, *178* (*1900*). — The method employed is a very ingenious one. The author passes an air current through a solution of hydrochloric acid and into water, measuring the increase in conductivity of the latter. In this way he determines the partial pressure of the hydrochloric acid. [It would seem simpler to distil under diminished pressure and measure the conductivity of the resulting solution.] By shaking the hydrochlorid of an insoluble base with water and determining the amount of hydrochloric acid which goes into solution, the dissociation pressure of the hydrochlorid can be calculated. There is also a general discussion of vapor-pressure relations. *W. D. B.*

On colloidal cadmium. *G. Bredig. Zeit. phys. Chem.* 32, *127* (*1900*). — By passing an electric arc between cadmium electrodes in cooled air-free water, a colloidal solution of cadmium is obtained which can be preserved for a long time if kept away from the air. Electrolytes cause coagulation. Colloidal zinc can also be prepared, but is much less stable than the cadmium solution.

W. D. B.

On colloidal solutions. *G. Bredig and A. Coehn. Zeit. phys. Chem.* 32, *129* (*1900*). — It is claimed that the results of Stoeckl and Vanino (4, 319) are not new, and that their conclusions are mostly wrong. *W. D. B.*

Remarks on the article: On the nature of so-called colloidal solutions. *R.*

Zsigmondy. Zeit. phys. Chem. 33, *63* (*1900*). — The author takes issue with Stoeckl and Vanino (4, 319) as to colloidal solutions being merely suspensions. *W. D. B.*

Poly-Component Systems

Contribution to our knowledge of dineric equilibria in systems of salt, water, and alcohol. *B. R. de Bruyn. Zeit. phys. Chem.* 32, *63* (*1900*). — The systems studied were ethyl alcohol and water with sodium and with ammonium sulfate; potassium carbonate and water with methyl alcohol and with ethyl alcohol. A dineric boundary curve was determined in each case, and also a number of isotherms. With ammonium sulfate, alcohol, and water, two liquid phases are impossible below about +8°; with potassium carbonate, methyl alcohol, and water, below about −35°. It is to be regretted that the author did not determine at least one dineric isotherm with sufficient accuracy to enable one to tell whether a simple hyperbolic formula did or did not express the results. As it is, the data are admirable from a qualitative point of view, but tantalizing as regards quantitative theory. *W. D. B.*

On equilibria in the system: water, phenol, and tartaric or racemic acid. *F. A. H. Schreinemakers. Zeit. phys. Chem.* 33, *74* (*1900*). — It is shown that tartaric and racemic acids cause water and phenol to be less miscible, that this can be counterbalanced by rise of temperature, and that the two acids have the same quantitative effect. *W. D. B.*

Equilibria in the system: water, phenol, and acetone. *F. A. H. Schreinemakers. Zeit. phys. Chem.* 33, *78* (*1900*). — Addition of acetone to phenol decreases the solubility of water until a solution is reached at 30° containing phenol 64.0, acetone 18.1, water 17.9 parts. Addition of acetone to water decreases the solubility of phenol until a solution is reached containing water 84.7, acetone 11.5, phenol 3.8 parts. The author has determined a number of points on the dineric surface. He appends a brief summary of the results obtained in this and in preceding papers. *W. D. B.*

The hydrolysis of chlorin. *A. A. Jakowkin. Zeit. phys. Chem.* 29, *613* (*1899*). — If chlorin dissolves in water according to the equation

$$Cl_2 + H_2O \rightleftharpoons HClO + \overset{+}{H} + \overset{-}{Cl},$$

the ratio of the cube of the concentration of the decomposition products to the concentration of the chlorin should be constant; the addition of any acid or any chlorid should decrease the solubility; and hydrochloric acid should be doubly effective. All of these points have been confirmed, chiefly from a study of the distribution ratio with carbon tetrachlorid as the second liquid. *W. D. B.*

Velocities

On catalysis by neutral salts. *H. Euler. Zeit. phys. Chem.* 32, *348* (*1900*). — Measurements have been made to determine the accelerating effect of neutral salts on the rate of inversion of sugar. This effect is practically independent of the sugar concentration and decreases with increasing acid concentration. The author considers all reactions as ion reactions, and he therefore concludes that neutral salts increase dissociation. While this may be true, it is not necessarily true. The fallacy lies in the assumption that the change in the concentration of hydrogen as ion is the only factor. While it is true that the rate of inversion is approximately proportional to the concentration of hydrogen as ion, it does not follow that the proportionality factor is necessarily a constant under all circumstances. The addition of potassium chlorid to a hydrochloric acid solution increases the partial pressure of the acid and it is not at all improbable that it may affect the inverting power of hydrogen as ion.

W. D. B.

On the hydrolysis of salt solutions. *L. Bruner. Zeit. phys. Chem.* 32, *133* (*1900*). — The method used was the inversion of cane sugar. Stannic chlorid was completely hydrolyzed at a dilution of eight liters; zirconium tetrachlorid 35 percent decomposed at a hundred liters. The salts of iron, aluminium, uranium, and beryllium show 1–15 percent decomposition in fortieth-normal solution, the chlorids being hydrolyzed more than the sulfates. *W. D. B.*

Hydrolysis of polysaccharids and decomposition of esters due to the catalytic action of metals. *O. Sulc. Zeit. phys. Chem.* 33, *47* (*1900*). — Palladium powder retards the hydrolytic action of acids on saccharose, maltose, and raffinose. Mercury, copper, silver, osmium, palladium, rhodium and iridium retard the decomposition of amyl acetate by water, mercury having very little effect, and iridium a very marked one. *W. D. B.*

On the energy of some oxysulfuric acids. *F. Cojazzi. Gazz. chim Ital.* 30, *I*, *187* (*1900*). — From experiments with methyl acetate it appears that the methyl, ethyl, and isoamyl oxysulfuric acids are just a trifle less dissociated than the isomeric methyl, ethyl and isoamyl sulfuric acids. *W. D. B.*

The chemical dynamics of the acetone condensation. *K. Koelichen. Zeit. phys. Chem.* 33, *129* (*1900*). — Under the influence of alkalies, acetone changes partially and reversibly into diacetone alcohol, the equilibrium concentration of this latter decreasing with rising temperature. The decomposition of the diacetone alcohol gives satisfactory results for a monomolecular reaction. Hydroxyl as ion is the catalytic agent. *W. D. B.*

On the decomposition of sodium thiosulfate. *H. v. Oettingen. Zeit. phys. Chem.* 33, *1* (*1900*). — The time at which a sodium thiosulfate solution begins to cloud in presence of an acid can be represented by the formula

$$y = \frac{1}{A \log (1 + bx)},$$

where y is the time, and x the concentration of hydrogen as ion, while A and b are arbitrary constants. Addition of sodium sulfate retards the reactions, changing the values of A and b, but not the form of the expression. It was impossible to study equilibrium phenomena since secondary reactions occur.

W. D. B.

Studies on aminolysis. *H. Goldschmidt and R. M. Salcher. Zeit. phys. Chem.* 29, *89* (*1899*). — The rate of change of diazoamido compounds into amidoazo compounds in anilin solutions is proportional to the amount of acid added. If we add pyridin hydrochlorid and determine the reaction velocity, we can calculate the amount of hydrochloric acid which the anilin has taken from the pyridin — provided we assume that pyridin hydrochlorid itself has no action. In this way, the authors have determined the following order for certain bases, the weakest coming first: quinolin, pyridin, tribenzylamin, diethylbenzylamin, triethylamin. The order in aqueous solutions is the same, and the ratio of the coefficients in the two solvents approximates a constant. [It would be interesting to reverse the operation and to determine the effect of adding anilin hydrochlorid to a solution in pyridin.] *W. D. B.*

On the decomposition of organic halid compounds in amyl alcohol solution by sodium. *R. Löwenherz. Zeit. phys. Chem.* 32, *477* (*1900*). — When sodium is added to a solution of chlorbenzene in amyl alcohol, sodium amylate and sodium chlorid are formed. The author shows that the amount of sodium converted into chlorid can be represented by the equation.

$$\mathrm{KNa} = \log \frac{\mathrm{A}}{\mathrm{A} - x},$$

where A and A $- x$ are the initial and final concentrations of the halogen compounds, Na the weight in grams of sodium added, and K a constant. This is given as an empirical formula, though it might easily have been deduced.

W. D. B.

The chemical kinetics of reactions in gases. *M. Bodenstein. Zeit. phys. Chem.* 29, *147, 295, 315, 429, 665*; 30, *113* (*1899*). — In the first paper, which is purely introductory, the author discusses the experimental evidence in favor of the actual occurrence of false equilibrium; in the second paper, the author publishes data on the rate of formation and decomposition of hydriodic acid between 280° and 510°, showing that a formula can be written expressing the change with the temperature. The third paper contains measurements on the reaction between hydrogen and sulfur. The author's experiments show that the reaction runs to an end with the formation of hydrogen sulfid even at 234°. These results are in flat contradiction with those of Pélabon which indicated 'false equilibrium' below 215°. Bodenstein finds that the rate of formation is proportional to the first power of the hydrogen concentration, and the square root of the sulfur concentration.

In the fourth paper are data on the reaction between hydrogen and selenium, and, here again, no evidence of false equilibrium could be found. Solid selenium acts as a catalytic agent, the effect being proportional to the surface. By keeping the surface constant a very satisfactory reaction velocity constant was obtained.

In the fifth paper the author studies the combination of hydrogen and oxygen. He finds no evidence of false equilibrium; the reaction takes place practically exclusively at the surface of the containing vessel; the reaction is trimolecular.

The last paper deals with high temperature thermoregulators. From 100° to 340° a paraffin bath with mercury regulator gives good results. A bath of tin and lead may also be used between 275° and 340°. For highest temperatures the authors used a lead bath, the difference in expansion between a porcelain rod and the iron vessel being communicated by a lever to the place where the gas supply was to be regulated. [An electrical device would seem to have been simpler.] *W. D. B.*

The question of false 'equilibrium'. *P. Duhem. Zeit. phys. Chem.* 29, *711* (*1899*). — It is pointed out that the discrepancy between Pélabon's results and those of Bodenstein with hydrogen and sulfur (preceding review) is probably due to the fact that the amount of sulfur (unstated) taken by Bodenstein was too great and there was therefore absorption of hydrogen by liquid sulfur. *W. D. B.*

'False equilibria'. *M. Bodenstein. Zeit. phys. Chem.* 30, *567* (*1899*). — In this reply to Duhem (preceding review) the author admits that he took about twice as much sulfur as he should have done to make his results comparable with those of Pélabon, but claims that this is immaterial. The point made by the author, that it is legitimate to reason from experiments with catalytic agents to experiments without catalytic agents, is certainly wrong. *W. D. B.*

Electromotive Forces

On the nature of electrocapillary phenomena. *S. W. J. Smith. Zeit. phys. Chem.* 32, *433* (*1900*). — Emphasis is laid on the fact that the maximum surface-tension is different in potassium chlorid and in potassium iodid solutions. Consequently, the potential difference necessary to produce a maximun surface-tension cannot be the true potential difference between metal and electrolyte. The difference between the potential differences necessary to produce the same surface-tension on the descending branch of potassium chlorid and potassium iodid solutions is equal to the electromotive force of the cell Hg | KI | KCl | Hg. We are therefore justified in assuming that the potential difference between these solutions is zero. *W. D. B.*

On the electromotive behavior of silver fluorid and of fluorin. *R. Abegg and C. Immerwahr. Zeit. phys. Chem.* 32, *142* (*1900*). — In concentrated solutions, silver fluorid is dissociated to about the same extent as silver nitrate; in dilute solutions the conductivity is greater than it should be, indicating hydrolysis. A silver fluorid solution will dissolve perceptible amounts of silver oxid. The decomposition voltage of a fluorid is +0.45 volt higher than that of the corresponding chlorid. *W. D. B.*

On the electrolytic reduction of non-electrolytes. *F. Haber. Zeit. phys. Chem.* 32, *193* (*1900*). — The author considers the reducible non-electrolyte at the cathode as a depolarizer reacting with the hydrogen evolved at a rate which is proportional to the concentration of the non-electrolyte and of the hydrogen or sodium evolved. For constant potential, the current should be proportional to concentration of the non-electrolyte. If the hydrogen concentration in or at the surface of the electrode be considered, the two-thirds power of its concentration would be proportional to the current. Substituting the numerical values for R, T, etc., the author deduces a formula

$$E = 0.0436 \log_{10} \frac{I}{C_{NO_2}} - \text{const},$$

where I is the current and C_{NO_2} the concentration of nitrobenzene. The experiments were made in alcoholic potash solution with such a current that no hydrogen was evolved The potential measurements agreed fairly well with the theory. At the end of the paper there is a polemic against Binz.

W. D. B.

Electrolysis and Electrolytic Dissociation

On the reactions during the electrolytic reduction of nitrobenzene. *F. Haber and C. Schmidt. Zeit. phys. Chem.* 32, *27* (*1900*). — In Haber's general scheme (3, 63) for the reduction of nitrobenzene there is no place for the appearance of azobenzene and yet this substance can be made practically quantitatively by the electrolytic reduction of nitrobenzene under certain conditions. It is now shown that in alkaline solution hydrazobenzene reacts instantaneously with nitrobenzene, forming azobenzene and azoxybenzene. The azobenzene is therefore due to a secondary chemical reaction and is not the result of an electrolytic reduction at all. This removes the one serious objection to Haber's theory. *W. D. B.*

On the electrolytic potential and its use. *A. Schukarew. Zeit. phys. Chem.* 29, *726* (*1899*). — The author objects to the chemical potential as too arbitrary and therefore introduces a function which he calls the 'electrolytic potential' which he defines as "the work necessary to change the conductivity by unit amount". He then deduces a dilution law in the form $\frac{\lambda^2}{V} = \text{const.}$ Instead of showing that this is an improvement over previous dilution laws, he points out that the Ostwald dilution law reduces to this, provided we take $\lambda_\infty - \lambda$ as practically the same as λ_∞. A serious misprint in equation 10 will bother the reader temporarily.

W. D. B.

On the relation between the dissociation constants of weak acids and the hydrolysis of their alkali salts. *J. Walker. Zeit. phys. Chem.* 32, *137* (*1900*). — Taking the dissociation of water as 1.09×10^{-7} mol/liter and using the author's value for weak acids, it is shown that the hydrolysis found experimentally by Shields can be calculated with a very fair degree of accuracy.

W. D. B.

Volumetric experiments on the affinity between some acids and acids in methyl alcohol. *A. Minozzi. Gazz. chim. Ital.* 29, *I*, *421* (*1899*). — There is a volume change of 6.4–6.7 cc when KOH, NaOH, CH_3OK or CH_3ONa in methyl alcohol solution is neutralized by HCl or HBr. With trichloracetic acid the change is 2.1–2.3 cc; with dichloracetic acid 2.3–2.5 cc; with monochloracetic acid 1.6–1.7 cc; with acetic acid 1.4–1.5 cc. The affinity constants, as calculated from these data, differ markedly from those obtained from conductivity measurements.

W. D. B.

TOXIC ACTION OF ACID SODIUM SALTS ON LUPINUS ALBUS

BY LOUIS KAHLENBERG AND ROLLAN M. AUSTIN.

The toxic action of solutions of acids, salts, and bases upon *Lupinus albus* has been the subject of previous investigations.[1] The general result obtained, when stated in terms of the theory of electrolytic dissociation, is that the toxicity of a solution is equal to the sum of the poisonous properties of the ions and the undissociated molecules present. Hydrogen ions were found to have a strongly toxic action, a solution containing 1/6400 gram hydrogen ions per liter just permitting seedlings of *Lupinus albus* to survive. With the exception of acid potassium sulphate and acid potassium oxalate, no solutions of acid salts have been tested in the researches mentioned, as to their poisonous properties on plants. As the degree of hydrogen dissociation of acid sodium salts has been carefully investigated by means of the method of sugar inversion,[2] and as the coefficients of dissociation have been found to be surprisingly small, it was thought to be of interest to ascertain the toxic effects of solutions of acid sodium salts on *Lupinus albus* and to compare the results obtained with the coefficients of hydrogen dissociation. In this way an additional test of the applicability of the theory of electrolytic dissociation to the physiological phenomena in question would be secured.

Briefly stated, the method of experimentation consisted in raising seedlings of *Lupinus albus* having radicles of from 2 cm to 4 cm long. Fifteen millimeters from the tip of each root a fine

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[1] Kahlenberg and True. Botanical Gazette, 22, 81 (1896). Heald. Ibid. 22, 125 (1896). True. Amer. Jour. Sci. 9, 183 (1900).

[2] J. E. Trevor. Zeit. phys. Chem. 10, 32 (1892). Also W. A. Smith. Zeit. phys. Chem. 25, 217 (1898).

mark was made with India ink. These seedlings were then suspended in the solution to be tested, so that the root, — and this only, — was immersed. After about 24 hours the seedlings were measured and their general condition was noted. In cases where it was doubtful as to whether the plant was dead or alive, the latter was returned to the solution and measured again later. The object of the whole procedure was to ascertain as nearly as possible the strength of the solution in which the seedlings would just survive. It is, of course, not possible to determine this strength to a high degree of accuracy as some seedlings, even when taken from the same lot, are more hardy and resistant than others. A fair degree of approximation, however, can be reached by testing several seedlings in each solution and by performing several series of tests with different lots of beans. A comparison of the results tabulated below will give an idea of the relative accuracy that may be obtained in experiments of this kind. This short description of the experimental method employed may here suffice as a more detailed one has already been published.[1]

The toxic action of acids and acid salts is best compared with that of hydrochloric acid, which, at the high dilution in which the seedlings just survive, is practically completely dissociated according to the dissociation theory. It is evident therefore that it is highly desirable to determine as accurately as possible this particular critical concentration for hydrochloric acid. In the previous researches,[2] the successive solutions tested differed in strength in that each was one-half as concentrated as the next preceding one. It is clear that by testing solutions that vary less in concentration, the critical strength sought might be more accurately ascertained. Accordingly, solutions of hydrochloric acid of suitable concentration were prepared and tested with seedlings of *Lupinus albus*. Four series of experiments were performed. The results are given in Table I.

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[1] Kahlenberg and True. l. c.; also Heald. l. c.

[2] l. c.

TABLE I

Hydrochloric Acid

(Begun Feb. 16, 11.20 a.m.; closed Feb. 17, 9.25 a.m.)

Concentration gm. mol. per liter	Length	Remarks
1/3200	16 mm	dead, flabby
"	16 "	" "
"	17 "	" "
"	17 "	" "
1/4000	16 "	" "
"	16 "	" "
"	17 "	" "
"	18 "	" "
1/4800	15 "	" "
"	17 "	" "
"	18 "	" "
"	19 "	alive (?) turgid
1/5600	18 "	dead, flabby
"	19 "	" "
"	21 "	alive, turgid
"	22 "	" "
1/6400	16 "	dead, flabby
"	19 "	alive, turgid
"	22 "	" "
"	23 "	" "

(Begun Feb. 19, 12.00 m.; closed Feb 20, 9.15 a.m.)

1/4000	15 mm	dead, flabby
"	15 "	" "
1/4800	16 "	" "
"	17 "	" "
"	17 "	" "
"	20 "	" "
1/5600	16 "	" "
"	17 "	" "
"	19 "	" "
"	21 "	alive, turgid
1/6400	17 "	dead, flabby
"	18 "	" "
"	19 "	alive, turgid
"	21 "	" "

(Begun March 12, 9.30 a.m.; closed March 13, 9.00 a.m.)

1/4000	16 mm	dead, flabby
"	17 "	" "
"	17 "	" "
"	21 "	alive (?) turgid
1/4800	16.5 "	dead, flabby
"	17 "	" "
"	19 "	" "
"	20 "	" "
1/5600	16 "	alive, turgid
"	19 "	" "
"	23 "	" "
"	24 "	" "
1/6400	20 "	" "
"	24 "	" "
"	24 "	" "
"	25 "	" "

(Begun March 12, 9.30 a.m.; closed March 13, 9.00 a.m.)

1/4000	15 mm	dead, flabby
"	16 "	" "
"	16 "	" "
"	17 "	" "
1/4800	17 "	" "
"	17 "	" "
"	17 "	" "
"	21 "	alive, turgid
1/5600	20 "	" "
"	24 "	" "
"	26 "	" "
"	28 "	" "
1/6400	18 "	" "
"	20 "	" "
"	20 "	" "
"	26 "	" "

From the third and fourth series in Table I, it appears that the seedlings survive in *n*/5600 solution. The first series shows that two beans died in the *n*/5600 solution, while two survived; the second series indicates that only one out of four seedlings survived in the *n*/5600 solution, and that two out of four survived in the *n*/6400 solution. From the second series one would conclude that the result for the critical concentration previously found (*n*/6400) is about correct; however, the beans used in this series were hardly normal in their resisting power, because they were very slow in germinating, the temperature of the laboratory having been rather low at night because of very cold weather. More weight is to be given to the results in the last two series, because the seedlings used were better average specimens. The results in these series and also those in the first series indicate that the previous result *n*/6400, while not far from correct, is rather low, and that *n*/5600 is probably the more correct value for the critical concentration.

The solutions of the acid sodium salts were prepared in each case by adding the calculated volume of a standard solution of pure sodium hydroxide to the acid and then diluting to the required volume. Table II gives the results obtained in four series of experiments on acid sodium oxalate.

TABLE II

Acid Sodium Oxalate

(Begun Feb. 20, 2.30 p.m.; closed Feb. 21, 9.15 a.m.)

Concentration in gm. mol. per liter	Length	Remarks
1/2800	16 mm	dead, flabby
''	16 ''	'' ''
1/3000	16 ''	'' ''
''	17 ''	'' ''
1/3200	17 ''	'' ''
''	18 ''	alive, tip dead
1/3600	17 ''	alive, turgid
''	19 ''	'' ''

(Begun Feb. 28, 3.30 p.m.; closed March 1, 2.00 p.m.)

1/2800	15 mm	dead, flabby
''	16 ''	'' ''
1/3000	15 ''	'' ''
''	16 ''	'' ''
1/3200	16 ''	'' ''
''	16.5 ''	'' ''
''	17 ''	alive, turgid
''	18 ''	'' ''

(Begun Feb. 28, 3.30 p.m. ; closed March 1, 2.00 p.m.)

1/3400	18 "	" "
"	20 "	" "
"	22 "	" "
"	23 "	" "
1/3600	19 "	" "
"	20 "	" "
"	21 "	" "
"	24 "	" "

(Begun March 2, 11.00 a.m.; closed March 3, 9.40 a.m.)

1/3000	15 mm	dead, flabby
"	18 "	" "
"	20 "	alive (?), turgid
"	21 "	" "
1/3200	18 "	dead, flabby
"	18 "	" "
"	21 "	" "
"	18 "	" "
1/3400	17 "	" "
"	17 "	alive, turgid
"	17 "	" "
"	22 "	" "
1/3600	19 "	" "
"	20 "	" "
"	21 "	" "
"	22 "	" "

(Begun March 9, 10.45 a.m.; closed March 10, 9.15 a.m.)

1/2800	16 mm	dead, flabby
"	17 "	" "
"	17 "	" "
"	17 "	" "
1/3000	16 "	" "
"	17 "	" "
"	17 "	" "
"	23 "	alive, turgid
1/3200	17 "	dead, flabby
"	18 "	alive, turgid
"	19 "	" "
"	19 "	" "
1/3400	17 "	dead, flabby
"	19 "	alive, turgid
"	20 "	" "
"	23 "	" "

The results in Table II show that the concentration in which the plants just survive is from *n*/3200 to *n*/3400.[1] Some more hardy plants do survive in the former concentration and, again, less resistant specimens occasionally die in the weaker solution. The concentration *n*/3400 will be taken as being more nearly the correct value sought.

Four series of tests were made with acid sodium tartrate, the results of which are given in Table III.

TABLE III

Acid Sodium Tartrate

(Begun Jan. 29, 12.00 m.; closed Jan. 30, 12.00 m.)

Concentration in gm. mol. per liter	Length	Remarks
1/1800	20 mm	dead, flabby
"	25 "	alive (?), turgid
1/2000	22 "	dead, flabby
"	22 "	" "
1/2200	30 "	alive, turgid
"	31 "	" "
1/2400	24 "	" "
"	33 "	" "
1/2600	24 "	" "
"	26 "	" "
1/2800	26 "	" "
"	29 "	" "
(Begun Feb. 28, 11.45 a.m.; closed March 1, 12.00 m.)		
1/1800	15 mm	dead, flabby
"	15 "	" "
"	15 "	" "
1/2000	15 "	" "
"	15 "	" "
"	16 "	" "
"	15 "	" "
1/2200	15 "	" "
"	15 "	" "
"	20 "	alive, turgid
1/2400	17 "	dead, flabby
"	17 "	" "
"	18 "	" "
"	18 "	alive, turgid
1/2600	16 "	dead, flabby
"	17 "	" "

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[1] In this article, the term *normal* always signifies a solution containing one gram molecule of the substance per liter.

(Begun March 2, 10.00 a.m.; closed March 3, 9.15 a.m.)

1/2000	17 mm	dead, flabby
"	17 "	" "
"	18 "	" "
"	19 "	" "
1/2200	16 "	" "
"	16.5 "	" "
"	17 "	" "
1/2400	17 "	" "
"	18 "	" "
"	18 "	" "
"	18 "	alive, turgid
1/2600	18 "	" "
"	18 "	" "
"	19 "	" "
"	19 "	" "
1/2800	17 "	" "
"	19 "	" "
"	19 "	" "
"	22 "	" "

(Begun March 9, 10.00 a.m.; closed March 10, 9.00 a.m.)

1/2000	15 mm	dead, flabby
"	15 "	" "
"	16 "	alive (?), turgid
"	17 "	dead, flabby
1/2200	15 "	" "
"	16 "	" "
"	17 "	" "
"	17 "	" "
1/2400	15 "	" "
"	15 "	" "
"	15 "	" "
"	18 "	" "
1/2600	15 "	" "
"	16 "	" "
"	18 "	" "
"	19 "	alive, turgid

The first series of Table III places the limit at *n*/2200; according to the second series the seedlings do not survive in the concentration *n*/2600, while one specimen lived in the *n*/2200 and one in the *n*/2400 solutions. Again, according to the third series, the limiting concentration is fairly definitely determined to be *n*/2600, while the fourth series shows that *n*/2600 has killed three beans out of four. Thus the results obtained vary between *n*/2200 and *n*/2800. As the concentration in which the beans will just survive is the one sought, *n*/2800 will be the strength used in comparing the toxic action of this salt with the poisonous effects of the other salts investigated.

In the case of acid sodium malate only three series of tests were made ; the results of these tests are detailed in Table IV.

TABLE IV

Acid Sodium Malate

(Begun Feb. 12, 10.00 a.m.; closed Feb. 13, 8.40 a.m.)

Concentration in gm. mol. per liter	Length	Remarks
1/300	15 mm	dead, flabby
"	17 "	" "
1/350	16 "	" "
"	18 "	alive (?), turgid
1/400	15 "	dead, flabby
"	18 "	" "
1/450	16.5 "	" "
"	17 "	" "
1/500	15 "	" "
"	17 "	" "
1/600	21 "	alive, turgid
"	21 "	" "

(Begun Feb. 14, 11.40 a.m.; closed Feb. 15, 9.25 a.m.)

1/400	19 mm	dead, flabby
"	18 "	" "
1/450	21 "	alive, turgid
"	21 "	" "
1/500	19 "	dead, flabby
"	20 "	alive, turgid
1/600	17 "	dead, flabby
"	18 "	" "

(Begun March 8, 9.25 a.m.; closed March 9, 9.00 a.m.)

1/400	17 mm	dead, flabby
"	17 "	" "
"	18 "	alive, turgid
"	22 "	" "
1/500	20 "	" "
"	21 "	" "
"	23 "	" "
"	23 "	" "
1/600	17 "	dead, flabby
"	21 "	alive, turgid
"	22 "	" "
"	22 "	" "

According to the first series, the limiting concentration sought for acid sodium malate is *n*/600. No definite conclusions can be drawn from the second series. It must be stated in this connection, however, that the specimens used in this series varied more from each other in their development than usual. The seedlings used in the third series were a much better average lot than those employed in either of the two other series; therefore, much more reliance is to be placed on the results recorded in the last series. According to the third series, the concentration in which the seedlings will survive may safely be placed at *n*/500.

On sodium acid succinate four series of tests were made. The data obtained are given Table V.

TABLE V

Acid Sodium Succinate

(Begun Feb. 10, 11.00 a.m.; closed Feb. 11, 10.00 a.m.)

Concentration in gm. mol. per liter	Length	Remarks
1/80	24 mm	dead, flabby
"	27 "	" "
1/100	23 "	alive, turgid, discolored
"	25 "	" " "
1/120	25 "	" " "
"	28 "	" " "
1/140	28 "	alive, turgid
"	30 "	" "
1/160	27 "	" "
"	29 "	" "

(Begun Feb. 12, 11.00 a.m.; closed Feb. 13, 8.00 a.m.)

1/80	15 mm	dead, flabby
"	24 "	alive, turgid
1/100	15 "	dead, flabby
"	20 "	alive, turgid
1/120	18 "	" "
"	19 "	" "
1/160	16 "	" "
"	17 "	" "

(Begun Feb. 14, 3.30 p.m.; closed Feb. 15, 3.30 p.m.)

1/60	18 mm	dead, flabby
"	18 "	" "
1/80	19 "	" "
"	24 "	" "
1/100	23 "	" "
"	25 "	" "
1/120	23 "	alive, turgid
"	24 "	" "
1/150	20 "	alive (tip dead)
"	22 "	alive, turgid

(Begun March 8, 2.20 p.m.; closed March 9, 4.00 p.m.)

1/80	18 mm	dead
"	23 "	dead, flabby
"	23 "	" "
"	24 "	" "
1/100	22 "	alive, turgid
"	22 "	" "
"	29 "	" "
"	30 "	" "
1/120	24 "	" "
"	24 "	" "
"	24 "	" "
"	25 "	" "
1/140	20 "	" "
"	21 "	" "
"	23 "	" "
"	26 "	" "

From Table V it appears that all the seedlings tested survived in the *n*/120 solution. In the first and fourth series, the plants also lived in the *n*/100 solution; but in the third series they were killed by the latter concentration, while in the second series one of the beans died and the other survived. In the comparison to be made hereafter *n*/120 will be used as the concentration in which the seedlings will survive.

Two experiments were performed on mono-sodium citrate. Table VI gives the results obtained.

Table VI

Mono-Sodium Citrate

(Begun Jan. 30, 4.00 p.m.; closed Jan. 31, 11.45 a.m.)

Concentration in gm. mol. per liter	Length	Remarks
1/1200	16 mm	dead, flabby
"	17 "	" "
1/1400	15 "	" "
"	19 "	" "
1/1600	16 "	" "
"	18 "	" "
1/1800	21 "	alive, turgid
"	22 "	" "
(Begun March 5, 9.30 a.m.; closed March 6, 9.30 a.m.)		
1/1200	16 mm	dead, flabby
"	18 "	alive (?) turgid
1/1400	16 "	dead, flabby
"	16 "	" "
"	18 "	" "
"	18 "	" "
1/1600	16 "	" "
"	17 "	" "
"	17 "	" "
"	22 "	alive turgid
1/1800	17 "	" "
"	17 "	" "
"	18 "	" "
"	21 "	" "
1/2000	19 "	" "
"	21 "	" "
"	21 "	" "
"	22 "	" "

From Table VI it is evident that the critical strength of the solution for mono-sodium citrate is *n*/1800, for all the seedlings tested survived in this concentration, while with one exception they died in the *n*/1600 solution.

The three series of experiments made with di-sodium citrate are recorded in Table VII. In the stronger concentrations used, this salt has the tendency to turn the rootlets brown.

TABLE VII

Di-Sodium Citrate

(Begun Jan. 30, 4.40 p.m.; closed Jan. 31, 12.00 m.)

Concentration in gm. mol. per liter	Length	Remarks
1/300	17 mm	dead, flabby, brown
"	18 "	" " "
1/350	16 "	" " "
"	17 "	" " "
1/400	17 "	dead, flabby
"	20 "	" "
1/500	17 "	alive, turgid
"	21 "	" "
1/600	15 "	accidentally injured
"	22 "	alive, turgid
(Begun Feb. 16, 3.30 p.m.; closed Feb. 17, 12.40 p.m.)		
1/300	18 mm	dead, flabby, brown
"	18 "	" " "
1/350	18 "	" " "
"	19 "	" " "
1/400	20 "	alive, turgid
"	22 "	" "
"	22 "	" "
"	23 "	" "
1/450	20 "	" "
"	20 "	" "
"	21 "	" "
"	21 "	" "
1/500	22 "	" "
"	22 "	" "
"	23 "	" "
"	23 "	" "
1/600	22 "	" "
"	22 "	" "
(Begun March 6, 2.00 p.m.; closed March 7, 4.30 p.m.)		
1/300	15 mm	dead, flabby
"	15 "	" "
1/350	15 "	alive (?) turgid
"	19 "	alive, turgid
"	19 "	" "
"	27 "	" "

(Begun March 6, 2.00 p.m.; closed March 7, 4.30 p.m.)

1/400	17 mm.	alive, turgid
"	20 "	" "
"	20 "	" "
"	21 "	" "
1/450	19 "	" "
"	21 "	" "
"	23 "	" "
"	24 "	" "
1/500	18 "	" "
"	22 "	" "

The first series of Table VII would indicate the critical concentration to be *n*/500; according to the second series it is *n*/400, while the third series would place it at *n*/350. As more seedlings were tested in each of the second and third series than in the first, *n*/400 will be taken as the concentration of di-sodium citrate in which the seedlings will just survive.

The results of the foregoing investigations have been collected in Table VIII, the headings of which give the explanations necessary to understand the table. With the single exception of the value for sodium acid oxalate, the figures of column 4 are taken from Smith's determinations.[1]

The normal sodium salts of the acids employed in making the acid salts tested in Table VIII have only a very slight toxic action, if any. The toxic effect of the free acids has been previously determined approximately by Kahlenberg and True.[2] The results that were obtained are collected in Table IX.

While the data in Table IX can at best give only a rough idea between what limits the critical concentration for each acid lies, they do show that the free acids have a highly poisonous effect. A comparison of Table IX with the second column of Table VIII, shows that the acid salts are less toxic than the free acids, but not surprisingly so. The toxicity of acid sodium malate and acid sodium succinate differs more, relatively, from that of malic and succinic acids, respectively, than does the toxic-

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[1] l. c.

[2] l. c.

TABLE VIII

Substance	No of liters in which 1 gm. mol. must be dissolved in order that *Lupinus albus* may survive in the solution.	Percent H dissociation as determined by toxic action, assuming HCl to be completely dissociated in n/5600 solution.	Percent of H dissociation in solutions containing 1 gm. mol. in 128 liters, as determined by sugar inversion experiments.	According to inversion tests a solution of 1 gm. mol. per 128 liters, therefore, contains 1 gm. H ions in
Hydrochloric acid	5600	100.0	——	——
Sodium acid oxalate	3400	60.7	4.37	2929 liters
Sodium acid tartrate	2800	50.0	2.8	4571 "
Sodium acid malate	500	8.9	0.719	17800 "
Sodium acid succinate	120	2.1	0.159	80500 "
Mono-sodium citrate	1800	31.1	1.92	6666 "
Di-sodium citrate	400	7.1	0.06	21333 "

TABLE IX

Substance	Seedlings were killed by a solution containing 1 gm. equiv. in	Seedlings survived in a solution containing 1 gm. equiv. in
Oxalic acid	3200 liters	6400 liters
Tartaric acid	3200 "	6400 "
Malic acid	1600 "	3200 "
Citric acid	1600 "	3200 "
Succinic acid	800 "	1600 "

ity of acid sodium oxalate and acid sodium tartrate from the poisonous action of the corresponding free acids.

Heretofore the poisonous action of the acids has been ascribed mainly to the hydrogen ions present. If it be assumed that the hydrogen ions cause the poisonous effect observed in the case of acid salts, it is evident from the last two columns of Table VIII that, with the single exception of acid sodium oxalate, all the acid salts mentioned ought to permit *Lupinus albus* to survive in solutions containing 1 gm. mol. in 128 liters. Now, only acid sodium succinate allows the seedlings to grow in the latter concentration, though according to the fifth column of Table VIII, the plants evidently ought to flourish in concentrations much stronger than *n*/120. For sodium acid oxalate, Trevor found the hydrogen dissociation to be 6.13 percent for a solution containing 1 gm. mol. in 256 liters; this means that 1 gm. H-ions would be contained in 4176 liters of the latter solution. Since it has been found that the seedlings will survive in a solution of 1 gm. mol. sodium oxalate in 3400 liters, it is evident that, if the toxicity be due only to the H-ions present, the plants ought to survive in a solution containing 1 gm. mol. in 256 liters. The great discrepancy between the actual facts and the theory that the toxicity is due to the H-ions is therefore manifest in the case of all these acid salts. This discrepancy is also strikingly shown by a comparison of the third column (of Table VIII) containing the degrees of dissociation, and the fourth column giving the results obtained by the method of sugar inversion. Of course, we here compare solutions of different strengths, but it is not at all probable that the H-dissociation of these acid salts would increase sufficiently with the dilution to harmonize the results given in the two columns last mentioned. This is evident, for instance, from the case of acid sodium succinate, where the concentrations are nearly comparable.

It will be noted that in general the order of the toxicity of the acid salts is also the order in which they invert sugar, with the single and striking exception that di-sodium citrate inverts sugar much more slowly than a corresponding solution of acid sodium succinate, yet the former has a much greater toxic action than the latter.

It is clear that these acid salts are much more poisonous than they ought to be, assuming their toxicity to be due to the hydrogen ions only. This really means then that the theory of electrolytic dissociation is unsatisfactory in explaining the toxic action of these acid salts. The true explanation of the poisonous action of these acid salts (and that of acids also) is very likely to be found in the property which they all have in common, namely, in their ability to neutralize basic substances; and of course, this action would depend on the avidity of the acid or acid salt employed. It is evident, however, that this explanation is independent of the theory of electrolytic dissociation. It was found by Kahlenberg[1] that solutions of acid salts also have a much more pronounced sour taste than they ought to have considering their taste to be due solely to the H-ions present, so that the results obtained are in a general way such as might have been expected.

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[1] Jour. Phys. Chem. 4, 331 (1900).

RELATIONSHIPS BETWEEN THERMODYNAMIC FUNDAMENTAL FUNCTIONS

BY J. E. TREVOR

I. Introduction

In reversible compression thermodynamics, two familiar 'differential properties of the thermodynamic potential H' are

$$\left.\begin{aligned} \frac{\partial}{\partial p} \cdot \frac{(H_2 - H_1)_{p,\theta}}{p} &= \frac{-W_{12}}{p^2}, \\ \frac{\partial}{\partial \theta} \cdot \frac{(H_2 - H_1)_{p,\theta}}{\theta} &= \frac{-Q_{12}}{\theta^2}; \end{aligned}\right\} \qquad (1)$$

in which equations p and θ denote the equilibrium values of the pressure and thermodynamic temperature, W_{12} and Q_{12} the work and heat absorbed by a body or system of bodies—a 'system'—in passing from a state 1 to another state 2, and H the thermodynamic potential

$$H(p, \theta) = E + pv - \theta\eta,$$

in which equation E, v, η denote, respectively, the energy, volume, and entropy of the system. The subscripts p, θ indicate that the change in question is effected at constant p, θ; and it is understood that no mass is added to or removed from the system during the operation. The question arises, whether there are other relations of the form of (1), and if so what they are.

II. Closed systems

In the reversible compression thermodynamics of a 'closed system' of phases, i. e., of a system of given masses, the differential of the energy of the system is given by the equation

$$dE = -pdv + \theta d\eta;$$

which relation, by means of the definition equations

$$\left.\begin{aligned} F &= E - \theta\eta \\ G &= E + pv \\ H &= E + pv - \theta\eta, \end{aligned}\right\} \tag{2}$$

may be expressed in the different ways:

$$\left.\begin{aligned} dE(v, \eta) &= -pdv + \theta d\eta \\ dF(v, \theta) &= -pdv - \eta d\theta \\ dG(p, \eta) &= vdp + \theta d\eta \\ dH(p, \theta) &= vdp - \eta d\theta. \end{aligned}\right\} \tag{3}$$

The answer to our question is to be sought by expressing each of the 'fundamental functions'

$$E, \quad F, \quad G, \quad H,$$

in terms of each of the others, and applying the results to changes between two different states of the closed system. We are, accordingly, to find the equations

$$\begin{array}{llll} E = E(F) & F = F(E) & G = G(E) & H = H(E) \\ = E(G) & = F(G) & = G(F) & = H(F) \\ = E(H), & = F(H), & = G(H), & = H(G); \end{array}$$

in which the indicated function in each case is to be understood as a function of the independently variable function, and of its derivatives and independent variables.

To this end we have, from the definition equations (2), the equations of the first column below; which become, by substitution of the partial derivatives that appear in the differential equations (3), the corresponding equations of the second column.

$$\left.\begin{array}{l|l} E = F + \theta\eta & E = F - \theta\dfrac{\partial F}{\partial \theta} \\[2ex] = G - pv & = G - p\dfrac{\partial G}{\partial p} \\[2ex] = H - pv + \theta\eta & = H - p\dfrac{\partial H}{\partial p} - \theta\dfrac{\partial H}{\partial \theta} \end{array}\right\} \tag{4a}$$

$$\begin{array}{l|l}
F = E - \theta\eta & F = E - \eta\dfrac{\partial E}{\partial \eta} \\
\quad = (G - pv) - \theta\eta & \quad = G - p\dfrac{\partial G}{\partial p} - \eta\dfrac{\partial G}{\partial \eta} \\
\quad = H - pv & \quad = H - p\dfrac{\partial H}{\partial p}
\end{array} \left.\vphantom{\begin{array}{l}a\\a\\a\end{array}}\right\} \quad (4b)$$

$$\begin{array}{l|l}
G = E + pv & G = E - v\dfrac{\partial E}{\partial v} \\
\quad = (F + \theta\eta) + pv & \quad = F - \theta\dfrac{\partial F}{\partial \theta} - v\dfrac{\partial F}{\partial v} \\
\quad = H + \theta\eta & \quad = H - \theta\dfrac{\partial H}{\partial \theta}
\end{array} \left.\vphantom{\begin{array}{l}a\\a\\a\end{array}}\right\} \quad (4c)$$

$$\begin{array}{l|l}
H = E + pv - \theta\eta & H = E - v\dfrac{\partial E}{\partial v} - \eta\dfrac{\partial E}{\partial \eta} \\
\quad = F + pv & \quad = F - v\dfrac{\partial F}{\partial v} \\
\quad = G - \theta\eta. & \quad = G - \eta\dfrac{\partial G}{\partial \eta}.
\end{array} \left.\vphantom{\begin{array}{l}a\\a\\a\end{array}}\right\} \quad (4d)$$

It should be noted at this point that, because of the relation

$$E + H = F + G,$$

the long equation of each of the above four sets is equivalent to the sum of the other two that contain the same derivatives.

These twelve equations can be written more compactly. Each one has one or the other of the forms

$$\begin{aligned}
U &= V - x\frac{\partial V}{\partial x}, \\
U &= V - x\frac{\partial V}{\partial x} - y\frac{\partial V}{\partial y} \\
&= \left(V - x\frac{\partial V}{\partial x}\right) + \left(V - y\frac{\partial V}{\partial y}\right) - V;
\end{aligned}$$

which may be written

$$\left\{\begin{aligned}
U &= -x^2\frac{\partial}{\partial x}\cdot\frac{V}{x} \\
U &= -x^2\frac{\partial}{\partial x}\cdot\frac{V}{x} - y^2\cdot\frac{\partial}{\partial y}\,\frac{V}{y} - V.
\end{aligned}\right.$$

By means of these transformations, our equations take the forms:

$$
\begin{array}{l|l}
\mathrm{E} = -\theta^2\dfrac{\partial}{\partial\theta}\cdot\dfrac{\mathrm{F}}{\theta} & \mathrm{G} = -v^2\dfrac{\partial}{\partial v}\cdot\dfrac{\mathrm{E}}{v} \\
\phantom{\mathrm{E}} = -p^2\dfrac{\partial}{\partial p}\cdot\dfrac{\mathrm{G}}{p} & \phantom{\mathrm{G}} = -\theta^2\dfrac{\partial}{\partial\theta}\cdot\dfrac{\mathrm{F}}{\theta} - v^2\dfrac{\partial}{\partial v}\cdot\dfrac{\mathrm{F}}{v} - \mathrm{F} \\
\phantom{\mathrm{E}} = -p^2\dfrac{\partial}{\partial p}\cdot\dfrac{\mathrm{H}}{p} - \theta^2\dfrac{\theta}{\partial\theta}\cdot\dfrac{\mathrm{H}}{\theta} - \mathrm{H} & \phantom{\mathrm{G}} = -\theta^2\dfrac{\partial}{\partial\theta}\cdot\dfrac{\mathrm{H}}{\theta} \\
\mathrm{F} = -\eta^2\dfrac{\partial}{\partial\eta}\cdot\dfrac{\mathrm{E}}{\eta} & \mathrm{H} = -v^2\dfrac{\partial}{\partial v}\cdot\dfrac{\mathrm{E}}{v} - \eta^2\dfrac{\partial}{\partial\eta}\cdot\dfrac{\mathrm{E}}{\eta} - \mathrm{E} \\
\phantom{\mathrm{F}} = -p^2\dfrac{\partial}{\partial p}\cdot\dfrac{\mathrm{G}}{p} - \eta^2\dfrac{\partial}{\partial\eta}\cdot\dfrac{\mathrm{G}}{\eta} - \mathrm{G} & \phantom{\mathrm{H}} = -v^2\dfrac{\partial}{\partial v}\cdot\dfrac{\mathrm{F}}{v} \\
\phantom{\mathrm{F}} = -p^2\dfrac{\partial}{\partial p}\cdot\dfrac{\mathrm{H}}{p} & \phantom{\mathrm{H}} = -\eta^2\dfrac{\partial}{\partial\eta}\cdot\dfrac{\mathrm{G}}{\eta}\,.
\end{array}
$$

Discarding the redundant long equation of each set, and arranging the others with regard to the functions that are differentiated, we find the following general results:

$$
\begin{array}{ll|ll}
(\mathrm{E}) & \left\{\begin{array}{l} -v^2\dfrac{\partial}{\partial v}\cdot\dfrac{\mathrm{E}}{v} = \mathrm{G} \\[2ex] -\eta^2\dfrac{\partial}{\partial\eta}\cdot\dfrac{\mathrm{E}}{\eta} = \mathrm{F} \end{array}\right. & \left.\begin{array}{l} -p^2\dfrac{\partial}{\partial p}\cdot\dfrac{\mathrm{G}}{p} = \mathrm{E} \\[2ex] -\eta^2\dfrac{\partial}{\partial\eta}\cdot\dfrac{\mathrm{G}}{\eta} = \mathrm{H} \end{array}\right\} & (\mathrm{G}) \\[4ex]
(\mathrm{F}) & \left\{\begin{array}{l} -v^2\dfrac{\partial}{\partial v}\cdot\dfrac{\mathrm{F}}{v} = \mathrm{H} \\[2ex] -\theta^2\dfrac{\partial}{\partial\theta}\cdot\dfrac{\mathrm{F}}{\theta} = \mathrm{E} \end{array}\right. & \left.\begin{array}{l} -p^2\dfrac{\partial}{\partial p}\cdot\dfrac{\mathrm{H}}{p} = \mathrm{F} \\[2ex] -\theta^2\dfrac{\partial}{\partial\theta}\cdot\dfrac{\mathrm{H}}{\theta} = \mathrm{G}. \end{array}\right\} & (\mathrm{H})
\end{array}
$$

On effecting the indicated differentiations, we obtain, of course, our initial equations (4*a*) to (4*d*); of which the present equations are interesting forms.

The general results (E) to (H), when applied to changes in which the explicitly appearing independent variable is maintained constant in each case, become

$$
\left.\begin{array}{l}
-v^2\dfrac{\partial}{\partial v}\cdot\dfrac{(\mathrm{E}_2-\mathrm{E}_1)_v}{v} = (\mathrm{G}_2-\mathrm{G}_1)_v \\[2ex]
-\eta^2\dfrac{\partial}{\partial\eta}\cdot\dfrac{(\mathrm{E}_2-\mathrm{E}_1)_\eta}{\eta} = (\mathrm{F}_2-\mathrm{F}_1)_\eta
\end{array}\right\} \qquad (\mathrm{E}a)
$$

$$\left.\begin{aligned} -v^2\frac{\partial}{\partial v}\cdot\frac{(F_2-F_1)_v}{v} &= (H_2-H_1)_v \\ -\theta^2\frac{\partial}{\partial\theta}\cdot\frac{(F_2-F_1)_\theta}{\theta} &= (E_2-E_1)_\theta \end{aligned}\right\}\qquad(Fa)$$

$$\left.\begin{aligned} -p^2\frac{\partial}{\partial p}\cdot\frac{(G_2-G_1)_p}{p} &= (E_2-E_1)_p \\ -\eta^2\frac{\partial}{\partial\eta}\cdot\frac{(G_2-G_1)_\eta}{\eta} &= (H_2-H_1)_\eta \end{aligned}\right\}\qquad(Ga)$$

$$\left.\begin{aligned} -p^2\frac{\partial}{\partial p}\cdot\frac{(H_2-H_1)_p}{p} &= (F_2-F_1)_p \\ -\theta^2\frac{\partial}{\partial\theta}\cdot\frac{(H_2-H_1)_\theta}{\theta} &= (G_2-G_1)_\theta. \end{aligned}\right\}\qquad(Ha)$$

The correctness of these equations may be tested by executing the indicated differentiations. The first equation (E*a*), for example, becomes

$$-v\left(\frac{\partial E_2}{\partial v}-\frac{\partial E_1}{\partial v}\right)+(E_2-E_1)_v=(G_2-G_1)_v$$

$$v(p_2-p_1)+Q_{12}=(G_2-G_1)_v,$$

which is the result of integrating

$$dG=vdp+\theta d\eta$$

for constant volume. In this way, the eight equations are seen to give the corresponding integrations of the equations (3) for the differentials of the four 'fundamental functions.'

From the equations (F) to (H), further, we can derive four similar equations, when we note that a closed system can have different thermodynamic states with

different η at the same v, θ
" v " " p, η
" v " " p, θ
" η " " p, θ.

For this consideration makes it possible to apply four of the equations (E) to (H) to changes in which both independent variables of the differentiated function are maintained constant, and thus to obtain the equations

$$\begin{array}{l|l} (Fb)\ -\theta^2 \dfrac{\partial}{\partial \theta} \cdot \dfrac{(F_2-F_1)_{v,\theta}}{\theta} = Q_{12} & -p^2 \dfrac{\partial}{\partial p} \cdot \dfrac{(H_2-H_1)_{p,\theta}}{p} = W_{12} \\ (Gb)\ -p^2 \dfrac{\partial}{\partial p} \cdot \dfrac{(G_2-G_1)_{p,\eta}}{p} = W_{12} & -\theta^2 \dfrac{\partial}{\partial \theta} \cdot \dfrac{(H_2-H_1)_{p,\theta}}{\theta} = Q_{12}. \end{array} \left.\vphantom{\begin{array}{l}\dfrac{a}{b}\\ \dfrac{a}{b}\end{array}}\right\} (Hb)$$

The quantities $(E_2-E_1)_{v,\theta}$, $(E_2-E_1)_{p,\eta}$, $(F_2-F_1)_{p,\theta}$, $(G_2-G_1)_{p,\theta}$, have here been replaced by their values Q_{12}, W_{12}, W_{12}, Q_{12}. In these equations, the quantities

$$(F_2-F_1)_{v,\theta}$$
$$(G_2-G_1)_{p,\eta}$$
$$(H_2-H_1)_{p,\theta}$$

are, indeed, identically zero; but their indicated derivatives are not zero—they are either $-(\eta_2-\eta_1)$ or $+(v_2-v_1)$.

III. Individual phases

The equation for the differential of the energy of an individual phase of a system of phases is

$$dE = -pdv + \theta d\eta + \sum_1^n \mu dm,$$

the summation extending over the masses of the n independently variable components of the phase. This relation can be cast into the successive forms

$$\begin{aligned} dE &= -pdv + \theta d\eta + \Sigma\mu dm \\ d(E-\theta\eta) &= -pdv - \eta d\theta + \Sigma\mu dm \\ d(E+pv) &= vdp + \theta d\eta + \Sigma\mu dm \\ d(E+pv-\theta\eta) &= vdp - \eta d\theta + \Sigma\mu dm \end{aligned}$$

$$\begin{aligned} d(E-\Sigma\mu m) &= -pdv + \theta d\eta - \Sigma m d\mu \\ d(E-\theta\eta-\Sigma\mu m) &= -pdv - \eta d\theta - \Sigma m d\mu \\ d(E+pv-\Sigma\mu m) &= vdp + \theta d\eta - \Sigma m d\mu \\ d(E+pv-\theta\eta-\Sigma\mu m) &= vdp - \eta d\theta - \Sigma m d\mu; \end{aligned}$$

which equations are converted, by the definition equations

$$\left.\begin{array}{ll} & e = \mathrm{E} - \Sigma\mu m \\ \mathrm{F} = \mathrm{E} - \theta\eta & f = (\mathrm{E} - \theta\eta) - \Sigma\mu m \\ \mathrm{G} = \mathrm{E} + pv & g = (\mathrm{E} + pv) - \Sigma\mu m \\ \mathrm{H} = \mathrm{E} + pv - \theta\eta & h = (\mathrm{E} + pv - \theta\eta) - \Sigma\mu m, \end{array}\right\} \quad (5)$$

into the equilibrium equations

$$\left.\begin{array}{rl} d\mathrm{E}(v,\ \eta,\ m_1\ \ldots) = & -\,pdv + \theta d\eta + \Sigma\mu dm \\ d\mathrm{F}(v,\ \theta,\ m_1\ \ldots) = & -\,pdv - \eta d\theta + \Sigma\mu dm \\ d\mathrm{G}(p,\ \eta,\ m_1\ \ldots) = & \,vdp + \theta d\eta + \Sigma\mu dm \\ d\mathrm{H}(p,\ \theta,\ m_1\ \ldots) = & \,vdp - \eta d\theta + \Sigma\mu dm \\ de\,(v,\ \eta,\ \mu_1\ \ldots) = & -\,pdv + \theta d\eta - \Sigma m d\mu \\ df(v,\ \theta,\ \mu_1\ \ldots) = & -\,pdv - \eta d\theta - \Sigma m d\mu \\ dg(p,\ \eta,\ \mu_1\ \ldots) = & \,vdp + \theta d\eta - \Sigma m d\mu \\ dh(p,\ \theta,\ \mu_1\ \ldots) = & \,vdp - \eta d\theta - \Sigma m d\mu. \end{array}\right\} \quad (6)$$

These eight equations represent the general relation

$$d\mathrm{E} = -pdv + \theta d\eta + \sum \mu dm$$

successively in all the eight possible choices of sets of independent variables, taken three at a time from the pairs

$$p,\ v, \qquad \theta,\ \eta, \qquad \Sigma\mu,\ \Sigma m,$$

the members of no pair being taken together.

The energy E of the phase being a homogeneous function of the first degree of $v, \eta, m_1 \ldots$, we have, by Euler's theorem of homogeneous functions, the integral relation

$$\mathrm{E} = -pv + \theta\eta + \sum \mu m.$$

From this equation follows at once that our functions E ... h are respectively equal to the expressions set opposite them below:

$$
\begin{array}{ll|ll}
\mathrm{E} = & -pv + \theta\eta + \Sigma\mu m & e = & -pv + \theta\eta \\
\mathrm{F} = & -pv + \Sigma\mu m & f = & -pv \\
\mathrm{G} = & \theta\eta + \Sigma\mu m & g = & \theta\eta \\
\mathrm{H} = & \Sigma\mu m & h = & 0.
\end{array}
$$

Dropping from consideration the function h, i. e., dropping the equation

$$0 = v dp - \eta d\theta - \sum m d\mu,$$

our task is to express each of the functions $\mathrm{E} \ldots g$ in terms of each of the others and its independent variables and derivatives. We find, from the definition equations (5) and the derivatives that appear in equations (6), the following :

$$
\begin{array}{ll}
\mathrm{E} = \mathrm{F} + \theta\eta & = \mathrm{F} - \theta\dfrac{\partial \mathrm{F}}{\partial\theta} \\
\quad = \mathrm{G} - pv & = \mathrm{G} - p\dfrac{\partial \mathrm{G}}{\partial p} \\
\quad = \mathrm{H} - pv + \theta\eta & = \mathrm{H} - p\dfrac{\partial \mathrm{H}}{\partial p} - \theta\dfrac{\partial \mathrm{H}}{\partial\theta} \\
\quad = e + \sum\mu m & = e - \sum\mu\dfrac{\partial e}{\partial\mu} \\
\quad = f + \theta\eta + \sum\mu m & = f - \theta\dfrac{\partial f}{\partial\theta} - \sum\mu\dfrac{\partial f}{\partial\mu} \\
\quad = g - pv + \sum\mu m & = g - p\dfrac{\partial g}{\partial p} - \sum\mu\dfrac{\partial g}{\partial\mu}
\end{array}
$$

$$
\begin{array}{ll}
\mathrm{F} = \mathrm{E} - \theta\eta & = \mathrm{E} - \eta\dfrac{\partial \mathrm{E}}{\partial\eta} \\
\quad = \mathrm{G} - pv - \theta\eta & = \mathrm{G} - p\dfrac{\partial \mathrm{G}}{\partial p} - \eta\dfrac{\partial \mathrm{G}}{\partial\eta} \\
\quad = \mathrm{H} - pv & = \mathrm{H} - p\dfrac{\partial \mathrm{H}}{\partial p} \\
\quad = e - \theta\eta + \sum\mu m & = e - \eta\dfrac{\partial e}{\partial\eta} - \sum\mu\dfrac{\partial e}{\partial\mu} \\
\quad = f + \sum\mu m & = f - \sum\mu\dfrac{\partial f}{\partial\mu}
\end{array}
$$

$$= g - pv - \theta\eta + \sum \mu m = g - p\frac{\partial g}{\partial p} - \eta\frac{\partial g}{\partial \eta} - \sum \mu\frac{\partial g}{\partial \mu}$$

$$\begin{aligned}
G &= E + pv & &= E - v\frac{\partial E}{\partial v} \\
&= F + pv + \theta\eta & &= F - v\frac{\partial F}{\partial v} - \theta\frac{\partial F}{\partial \theta} \\
&= H + \theta\eta & &= H - \theta\frac{\partial H}{\partial \theta} \\
&= e + pv + \sum \mu m & &= e - v\frac{\partial e}{\partial v} - \sum \mu\frac{\partial e}{\partial \mu} \\
&= f + pv + \theta\eta + \sum \mu m & &= f - v\frac{\partial f}{\partial v} - \theta\frac{\partial f}{\partial \theta} - \sum \mu\frac{\partial f}{\partial \mu} \\
&= g + \sum \mu m & &= g - \sum \mu\frac{\partial g}{\partial \mu}
\end{aligned}$$

$$\begin{aligned}
H &= E + pv - \theta\eta & &= E = v\frac{\partial E}{\partial v} - \eta\frac{\partial E}{\partial \eta} \\
&= F + pv & &= F - v\frac{\partial F}{\partial v} \\
&= G - \theta\eta & &= G - \eta\frac{\partial G}{\partial \eta} \\
&= e + pv - \theta\eta + \sum \mu m & &= e - v\frac{\partial e}{\partial v} - \eta\frac{\partial e}{\partial \eta} - \sum \mu\frac{\partial e}{\partial \mu} \\
&= f + pv + \sum \mu m & &= f - v\frac{\partial f}{\partial v} - \sum \mu\frac{\partial f}{\partial \mu} \\
&= g - \theta\eta + \sum \mu m & &= g - \eta\frac{\partial g}{\partial \eta} - \sum \mu\frac{\partial g}{\partial \mu}
\end{aligned}$$

$$\begin{aligned}
e &= E - \sum \mu m & &= E - \sum m\frac{\partial E}{\partial m} \\
&= F + \theta\eta - \sum \mu m & &= F - \theta\frac{\partial F}{\partial \theta} - \sum m\frac{\partial F}{\partial m} \\
&= G - pv - \sum \mu m & &= G - p\frac{\partial G}{\partial p} - \sum m\frac{\partial G}{\partial m}
\end{aligned}$$

$$
\begin{aligned}
&= \mathrm{H} - pv + \theta\eta - \sum \mu m &&= \mathrm{H} - p\frac{\partial \mathrm{H}}{\partial p} - \theta\frac{\partial \mathrm{H}}{\partial \theta} - \sum m\frac{\partial \mathrm{H}}{\partial m}\\
&= f + \theta\eta &&= f - \theta\frac{\partial f}{\partial \theta}\\
&= g - pv &&= g - p\frac{\partial g}{\partial p}
\end{aligned}
$$

$$
\begin{aligned}
f &= \mathrm{E} - \theta\eta - \sum \mu m &&= \mathrm{E} - \eta\frac{\partial \mathrm{E}}{\partial \eta} - \sum m\frac{\partial \mathrm{E}}{\partial m}\\
&= \mathrm{F} - \sum \mu m &&= \mathrm{F} - \sum m\frac{\partial \mathrm{F}}{\partial m}\\
&= \mathrm{G} - pv - \theta\eta - \sum \mu m &&= \mathrm{G} - p\frac{\partial \mathrm{G}}{\partial p} - \eta\frac{\partial \mathrm{G}}{\partial \eta} - \sum m\frac{\partial \mathrm{G}}{\partial m}\\
&= \mathrm{H} - pv - \sum \mu m &&= \mathrm{H} - p\frac{\partial \mathrm{H}}{\partial p} - \sum m\frac{\partial \mathrm{H}}{\partial m}\\
&= e - \theta\eta &&= e - \eta\frac{\partial e}{\partial \eta}\\
&= g - pv - \theta\eta &&= g - p\frac{\partial g}{\partial p} - \eta\frac{\partial g}{\partial \eta}
\end{aligned}
$$

$$
\begin{aligned}
g &= \mathrm{E} + pv - \sum \mu m &&= \mathrm{E} - v\frac{\partial \mathrm{E}}{\partial v} - \sum m\frac{\partial \mathrm{E}}{\partial m}\\
&= \mathrm{F} + pv + \theta\eta - \sum \mu m &&= \mathrm{F} - v\frac{\partial \mathrm{F}}{\partial v} - \theta\frac{\partial \mathrm{F}}{\partial \theta} - \sum m\frac{\partial \mathrm{F}}{\partial m}\\
&= \mathrm{G} - \sum \mu m &&= \mathrm{G} - \sum m\frac{\partial \mathrm{G}}{\partial m}\\
&= \mathrm{H} + \theta\eta - \sum \mu m &&= \mathrm{H} - \theta\frac{\partial \mathrm{H}}{\partial \theta} - \sum m\frac{\partial \mathrm{H}}{\partial m}\\
&= e + pv &&= e - v\frac{\partial e}{\partial v}\\
&= f + \theta\eta + pv &&= f - \theta\frac{\partial f}{\partial \theta} - v\frac{\partial f}{\partial v}.
\end{aligned}
$$

All these equations have one or another of the forms

$$\left\{\begin{array}{l}
U = V - x\dfrac{\partial V}{\partial x} \\[2ex]
U = V - x\dfrac{\partial V}{\partial x} - y\dfrac{\partial V}{\partial y} \\[2ex]
U = V - \displaystyle\sum_{z_1}^{z_n} z\dfrac{\partial V}{\partial z} \\[2ex]
U = V - x\dfrac{\partial V}{\partial x} - \displaystyle\sum_{z_1}^{z_n} z\dfrac{\partial V}{\partial z} \\[2ex]
U = V - x\dfrac{\partial V}{\partial x} - y\dfrac{\partial V}{\partial y} - \displaystyle\sum_{z_1}^{z_n} z\dfrac{\partial V}{\partial z},
\end{array}\right.$$

which may be written, more compactly,

$$\left\{\begin{array}{l}
U = - x^2\dfrac{\partial}{\partial x}\cdot\dfrac{V}{x} \\[2ex]
U = - x^2\dfrac{\partial}{\partial x}\cdot\dfrac{V}{x} - y^2\dfrac{\partial}{\partial y}\cdot\dfrac{V}{y} - V \\[2ex]
U = - \displaystyle\sum_{z_1}^{z_n} z^2\dfrac{\partial}{\partial z}\cdot\dfrac{V}{z} - (n-1)V \\[2ex]
U = - x^2\dfrac{\partial}{\partial x}\cdot\dfrac{V}{x} - \displaystyle\sum_{z_1}^{z_n}\dfrac{\partial}{\partial z}\cdot\dfrac{V}{z} - nV \\[2ex]
U = - x^2\dfrac{\partial}{\partial x}\cdot\dfrac{V}{x} - y^2\dfrac{\partial}{\partial y}\cdot\dfrac{V}{y} - \displaystyle\sum_{z_1}^{z_n} z^2\dfrac{\partial}{\partial z}\cdot\dfrac{V}{z} - (n+1)V.
\end{array}\right.$$

By means of these transformations, our equations become the following; which are arranged in sets of six, each set representing all but one of the 'fundamental' functions E ... *g* in terms of that one and its derivatives and independent variables.

$$(\mathrm{E}')\quad\begin{cases}\mathrm{G} = -v^2\dfrac{\partial}{\partial v}\cdot\dfrac{\mathrm{E}}{v}\\[2ex] \mathrm{F} = -\eta^2\dfrac{\partial}{\partial \eta}\cdot\dfrac{\mathrm{E}}{\eta}\\[2ex] e = -\sum m^2\dfrac{\partial}{\partial m}\cdot\dfrac{\mathrm{E}}{m} - (n-1)\mathrm{E}\end{cases}$$

$$\mathrm{H} = -v^2\frac{\partial}{\partial v}\cdot\frac{\mathrm{E}}{v} - \eta^2\frac{\partial}{\partial \eta}\cdot\frac{\mathrm{E}}{\eta} - \mathrm{E} \qquad (\alpha)$$

$$g = -v^2\frac{\partial}{\partial v}\cdot\frac{\mathrm{E}}{v} - \sum m\frac{\partial}{\partial m}\cdot\frac{\mathrm{E}}{m} - n\mathrm{E} \qquad (\gamma)$$

$$f = -\eta^2\frac{\partial}{\partial \eta}\cdot\frac{\mathrm{E}}{\eta} - \sum m^2\frac{\partial}{\partial m}\cdot\frac{\mathrm{E}}{m} - n\mathrm{E} \qquad (\beta)$$

$$(\mathrm{F}')\quad\begin{cases}\mathrm{H} = -v^2\dfrac{\partial}{\partial v}\cdot\dfrac{\mathrm{F}}{v}\\[2ex] \mathrm{E} = -\theta^2\dfrac{\partial}{\partial \theta}\cdot\dfrac{\mathrm{F}}{\theta}\\[2ex] f = -\sum m^2\dfrac{\partial}{\partial m}\cdot\dfrac{\mathrm{F}}{m} - (n-1)\mathrm{F}\end{cases}$$

$$\mathrm{G} = -v^2\frac{\partial}{\partial v}\cdot\frac{\mathrm{F}}{v} - \theta^2\frac{\partial}{\partial \theta}\cdot\frac{\mathrm{F}}{\theta} - \mathrm{F} \qquad (\alpha)$$

$$e = -\theta^2\frac{\partial}{\partial \theta}\cdot\frac{\mathrm{F}}{\theta} - \sum m^2\frac{\partial}{\partial m}\cdot\frac{\mathrm{F}}{m} - n\mathrm{F} \qquad (\beta)$$

$$g = -v^2\frac{\partial}{\partial v}\cdot\frac{\mathrm{F}}{v} - \theta^2\frac{\partial}{\partial \theta}\cdot\frac{\mathrm{F}}{\theta} - \sum m^2\frac{\partial}{\partial m}\cdot\frac{\mathrm{F}}{m} - (n+1)\mathrm{F} \qquad (\delta)$$

$$(\mathrm{G}')\quad\begin{cases}\mathrm{E} = -p^2\dfrac{\partial}{\partial p}\cdot\dfrac{\mathrm{G}}{p}\\[2ex] \mathrm{H} = -\eta^2\dfrac{\partial}{\partial \eta}\cdot\dfrac{\mathrm{G}}{\eta}\\[2ex] g = -\sum m^2\dfrac{\partial}{\partial m}\cdot\dfrac{\mathrm{G}}{m} - (n-1)\mathrm{G}\end{cases}$$

$$F = -p^2 \frac{\partial}{\partial p} \cdot \frac{G}{p} - \eta^2 \frac{\partial}{\partial \eta} \cdot \frac{G}{\eta} - G \qquad (\alpha)$$

$$e = -p^2 \frac{\partial}{\partial p} \cdot \frac{G}{p} - \sum m^2 \frac{\partial}{\partial m} \cdot \frac{G}{m} - nG \qquad (\gamma)$$

$$f = -p^2 \frac{\partial}{\partial p} \cdot \frac{G}{p} - \eta^2 \frac{\partial}{\partial \eta} \cdot \frac{G}{\eta} - \sum m^2 \frac{\partial}{\partial m} \cdot \frac{G}{m} - (n+1)G \qquad (\delta)$$

$$(\mathrm{H}') \begin{cases} F = -p^2 \dfrac{\partial}{\partial p} \cdot \dfrac{H}{p} \\ G = -\theta^2 \dfrac{\partial}{\partial \theta} \cdot \dfrac{H}{\theta} \\ f = -p^2 \dfrac{\partial}{\partial p} \cdot \dfrac{H}{p} - \sum m^2 \dfrac{\partial}{\partial m} \cdot \dfrac{H}{m} - nH \end{cases}$$

$$E = -p^2 \frac{\partial}{\partial p} \cdot \frac{H}{p} - \theta^2 \frac{\partial}{\partial \theta} \cdot \frac{H}{\theta} - H \qquad (\alpha)$$

$$g = -\theta^2 \frac{\partial}{\partial \theta} \cdot \frac{H}{\theta} - \sum m^2 \frac{\partial}{\partial m} \cdot \frac{H}{m} - nH \qquad (\eta)$$

$$e = -p^2 \frac{\partial}{\partial p} \cdot \frac{H}{p} - \theta^2 \frac{\partial}{\partial \theta} \cdot \frac{H}{\theta} - \sum m^2 \frac{\partial}{\partial m} \cdot \frac{H}{m} - (n+1)H \qquad (\epsilon)$$

$$(e') \begin{cases} g = -v^2 \dfrac{\partial}{\partial v} \cdot \dfrac{e}{v} \\ f = -\eta^2 \dfrac{\partial}{\partial \eta} \cdot \dfrac{e}{\eta} \\ E = -\sum \mu^2 \dfrac{\partial}{\partial \mu} \cdot \dfrac{e}{\mu} - (n-1)e \end{cases}$$

$$G = -v^2 \frac{\partial}{\partial v} \cdot \frac{e}{v} - \sum \mu^2 \frac{\partial}{\partial \mu} \cdot \frac{e}{\mu} - ne \qquad (\gamma)$$

$$F = -\eta^2 \frac{\partial}{\partial \eta} \cdot \frac{e}{\eta} - \sum \mu^2 \frac{\partial}{\partial \mu} \cdot \frac{e}{\mu} - ne \qquad (\beta)$$

$$H = -v^2 \frac{\partial}{\partial v} \cdot \frac{e}{v} - \eta^2 \frac{\partial}{\partial \eta} \cdot \frac{e}{\eta} - \sum \mu^2 \frac{\partial}{\partial \mu} \cdot \frac{e}{\mu} - (n+1)e \qquad (\epsilon)$$

$$(f')\quad\begin{cases} e = -\theta^2 \dfrac{\partial}{\partial\theta} \cdot \dfrac{f}{\theta} \\[2ex] \mathrm{F} = -\sum \mu^2 \dfrac{\partial}{\partial\mu} \cdot \dfrac{f}{\mu} - (n-1)f \\[2ex] g = -v^2 \dfrac{\partial}{\partial v} \cdot \dfrac{f}{v} - \theta^2 \dfrac{\partial}{\partial\theta} \cdot \dfrac{f}{\theta} - f \end{cases}$$

$$\mathrm{H} = -v^2 \frac{\partial}{\partial v} \cdot \frac{f}{v} - \sum \mu^2 \frac{\partial}{\partial\mu} \cdot \frac{f}{\mu} - nf \qquad (\zeta)$$

$$\mathrm{E} = -\theta^2 \frac{\partial}{\partial\theta} \cdot \frac{f}{\theta} - \sum \mu^2 \frac{\partial}{\partial\mu} \cdot \frac{f}{\mu} - nf \qquad (\beta)$$

$$\mathrm{G} = -v^2 \frac{\partial}{\partial v} \cdot \frac{f}{v} - \theta^2 \frac{\partial}{\partial\theta} \cdot \frac{f}{\theta} - \sum \mu^2 \frac{\partial}{\partial\mu} \cdot \frac{f}{\mu} - (n+1)f \qquad (\delta)$$

$$(g')\quad\begin{cases} e = -p^2 \dfrac{\partial}{\partial p} \cdot \dfrac{g}{p} \\[2ex] \mathrm{G} = -\sum \mu^2 \dfrac{\partial}{\partial\mu} \cdot \dfrac{g}{\mu} - (n-1)g \\[2ex] f = -p^2 \dfrac{\partial}{\partial p} \cdot \dfrac{g}{p} - \eta^2 \dfrac{\partial}{\partial\eta} \cdot \dfrac{g}{\eta} - g \end{cases}$$

$$\mathrm{E} = -p^2 \frac{\partial}{\partial p} \cdot \frac{g}{p} - \sum \mu^2 \frac{\partial}{\partial\mu} \cdot \frac{g}{\mu} - ng \qquad (\gamma)$$

$$\mathrm{H} = -\eta^2 \frac{\partial}{\partial\eta} \cdot \frac{g}{\eta} - \sum \mu^2 \frac{\partial}{\partial\mu} \cdot \frac{g}{\mu} - ng \qquad (\eta)$$

$$\mathrm{F} = -p^2 \frac{\partial}{\partial p} \cdot \frac{g}{p} - \eta^2 \frac{\partial}{\partial\eta} \cdot \frac{g}{\eta} - \sum \mu^2 \frac{\partial}{\partial\mu} \cdot \frac{g}{\mu} - (n+1)g. \qquad (\delta)$$

In each of these seven sets, the equations are arranged in order with reference to the variables with respect to which the differentiations are successively indicated. The latter three of each set are sums of the former three; which is easily seen to follow from the relations

$$E + H = F + G \qquad (\alpha)$$

$$\begin{cases} E + f = e + F & (\beta) \\ E + g = e + G & (\gamma) \\ F + g = f + G & (\delta) \end{cases}$$

$$\begin{cases} H + e = G + f & (\epsilon) \\ H + f = F & (\zeta) \\ H + g = G, & (\eta) \end{cases}$$

which follow from the definition equations (5) and the relation

$$E + pv - \theta\eta - \Sigma\mu m = 0.$$

The relation that applies in each case is indicated by the appended Greek letter.

Discarding the three redundant equations of each set, our definitive results for individual phases are the twenty-one equations (E′) to (g'). These are in every way analogous to the corresponding general results (E) to (H) derived for closed systems. The application of them, as in the previous case, to finite reversible thermodynamic changes is too obvious to call for consideration in detail.

Cornell University, April, 1900.

THE BOILING-POINTS OF MIXTURES OF CHLORAL AND WATER

BY JOSEPH C. CHRISTENSEN

In May, 1899, I did some work at the suggestion of Dr. W. D. Bancroft on the boiling-points of mixtures of chloral and water. The results were rather unsatisfactory owing to the difficulty of obtaining concordant readings on the thermometer. The results are shown in plot No. 1 (curves 1 and 2 are from different settings of the Beckmann).

The difficulty mentioned, led to the adoption of a modification of the apparatus described by Bigelow in the American Chemical Journal of October, 1899. Fig. 1 shows the apparatus used in 1899; Fig. 2 that by which the accompanying results were obtained.

In practice, the current was usually kept at about 2.25 amp., but it was frequently increased during the experiment to 2.5 amp., or even more, without any change in the reading of the thermometer.

The following tables show the effect of varying the current and also the amount of liquid.

35 cc. water			50 cc. water		
Barom.	Temp.	Current	Barom.	Temp.	Current
755.0	5.17°	2.25	755.0	4.96° [1]	2.25
755.0	5.18	2.25	755.0	4.98 [1]	2.25
755.0	5.20	2.25	755.0	4.95 [1]	2.25
755.0	5.22	2.25	755.0	4.87 [1]	2.25
755.0	5.24	2.25	755.0	5.18	2.50
755.0	5.25	2:25	755.0	5.23	2.50
755.0	5.25	2.25	755.0	5.25	2.50
755.0	5.25	2.50	755.0	5.26	2.50
755.0	5.26	2.50	755.0	5.25	2.50
755.0	5.25	2.50	755.0	5.26	2.75
755.0	5.25	2.50	755.0	5.25	2.75

---

[1] Does not boil.

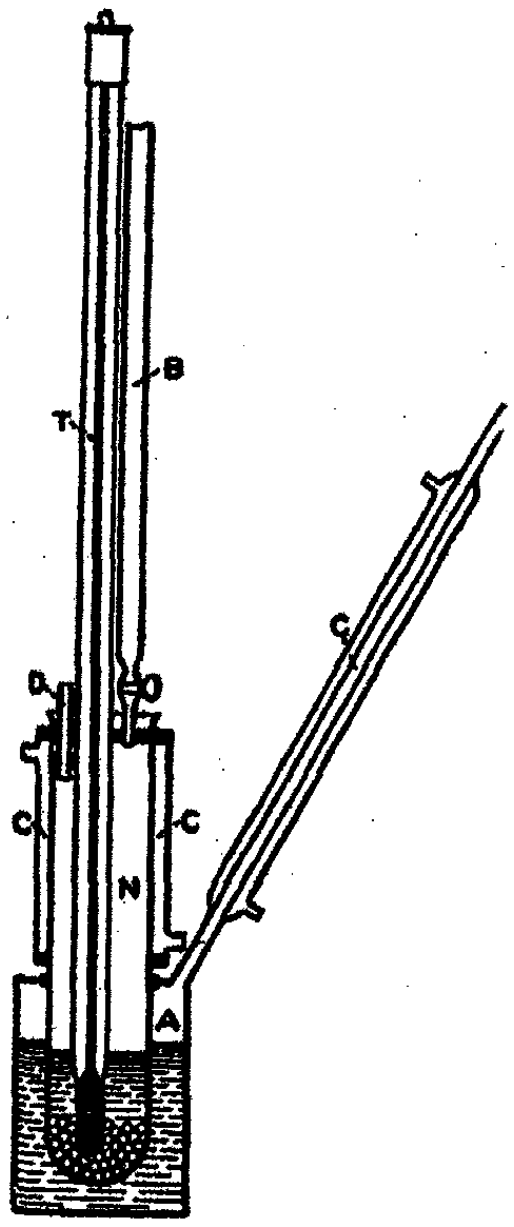

Fig. 1

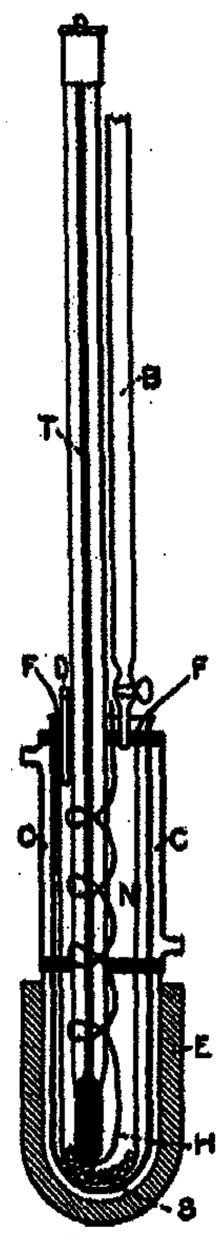

Fig. 2

A is a bath of brine.
B is a burette.
C, C, are condensers.
D is an open tube communicating with the air.
E is an asbestos jacket.
F, F, are terminals of the spiral.
S is a platinum spiral of about 15 ohms resistance, connecting with the power circuit.
H is a small watch-glass supported by a platinum wire sealed into it. It protects the thermometer from superheated vapor.
T is a Beckmann thermometer.
N is a test-tube 1¼ by 8 in.

The temperature in this, as in all the work, was taken every five minutes. This table shows that the apparatus is all that could be desired. The only disadvantage was that it would not work with over 60 cc liquid.

The break between curves No. 1 and No. 2, plot 2, is due probably to the impurity noted at this point. Curve No. 2, plot 1, probably represents the true conditions at this point. The drop in curve No. 3, plot 2, I am unable to explain. This curve was plotted from Table VII.

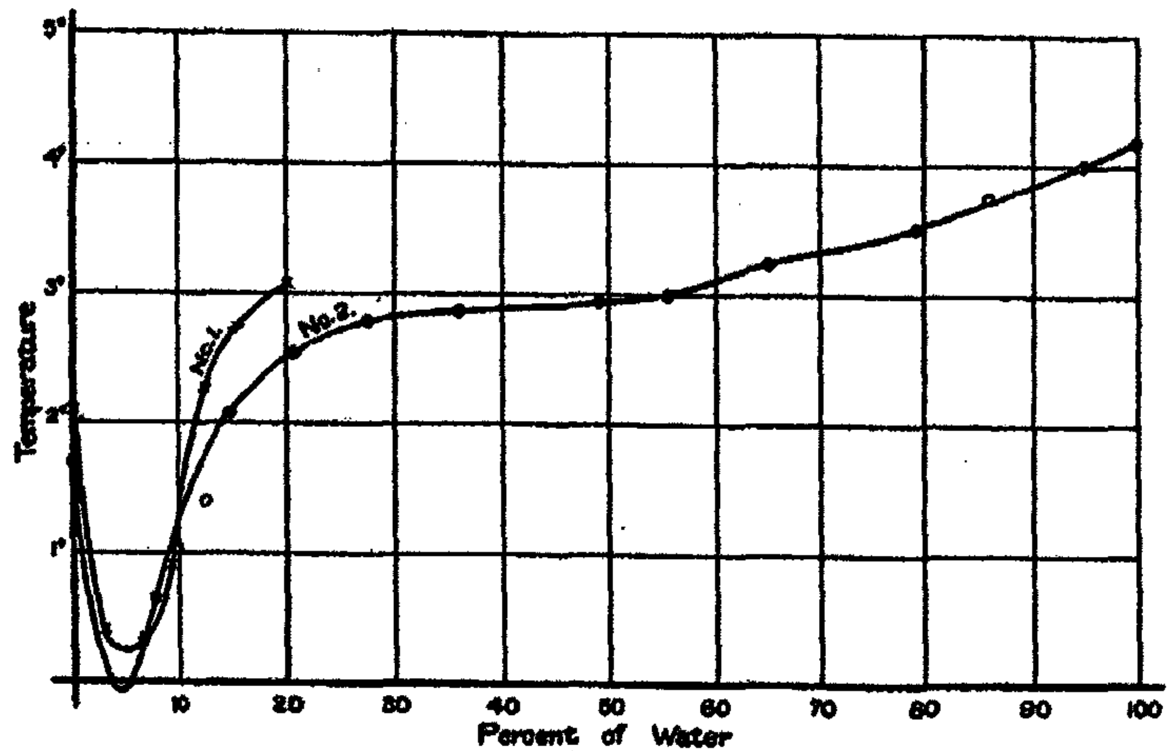

Plate I

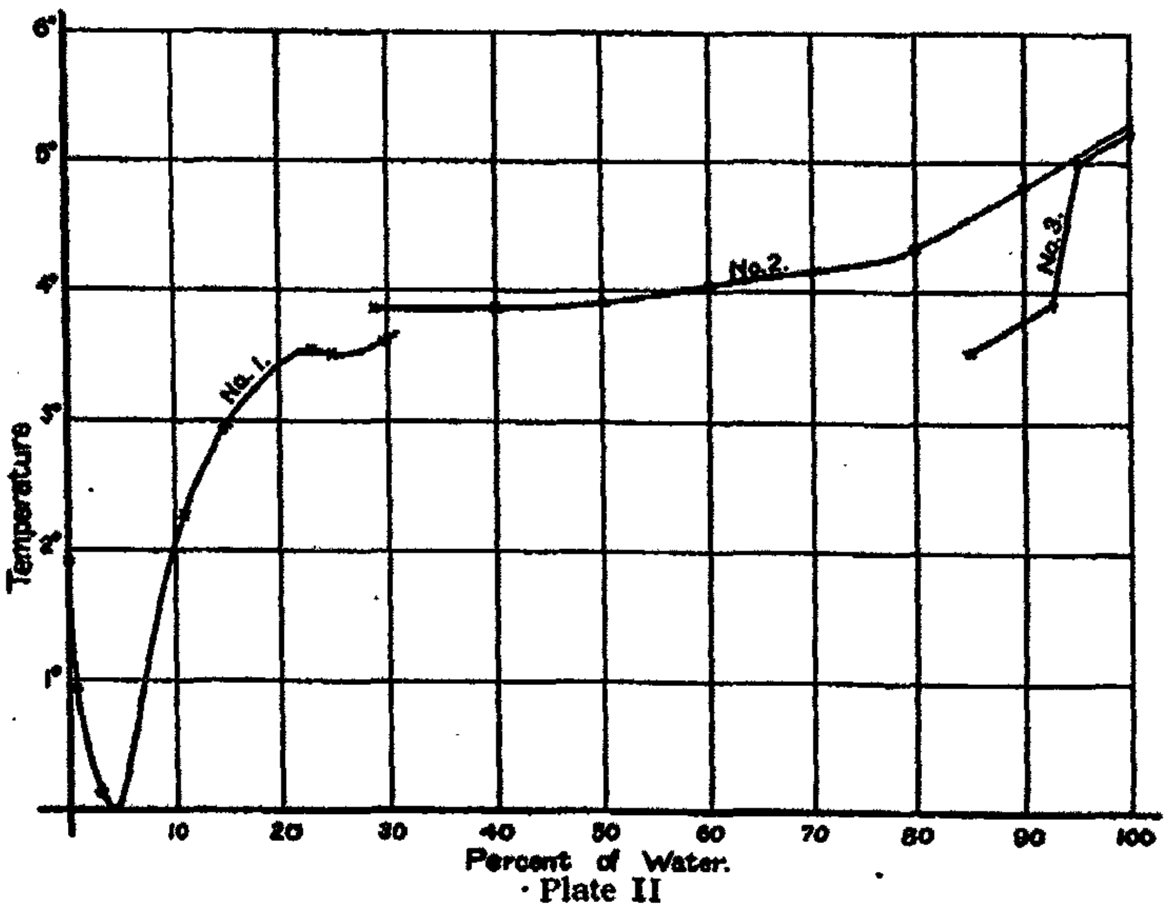

Plate II

TABLE I

Started with 53.4 grams pure chloral and added water from burette.
C = 2.5 amp.

	Barometer	Observed temp.	Temp. cor. to barom. = 755	Burette	Vol. water	Pct. water
*1	758.70	2.18		3.85	0	0
2		2.10		"	0	0
3		2.09		"	0	0
4	758 80	2.06		"	0	0
5		2.05		"	0	0
6		2.05	1.90°	"	0	0
7	758.90	1.44		4.00	0.15	0.28
8		1.50		"	"	"
9		1.48	1.34	"	"	"
10	759.00	1.23		4.10	0 25	0.46
11		1.26	1.10	4.10	"	"
12		1.00		4.20	0.35	0.65
*13	759.00	1.10	0.97	"	"	"
14		1.13		"	"	" [1]
15		0.92		4.30	0.45	0.84
16	758.85	0.98	0.83	"	"	"
17		0.98		"	"	"
18		0.79		4.40	0.55	1.02
19	758.80	0.85	0.70	"	"	"
20		0.85		"	"	"
21	754.00	0.90		4.7	0.55	1.02
22		0.74		"	"	" [2]
23		0.73	0.77	"	"	"
24		0.72		"	"	"
25		0.62		4.8	0.65	1.20
26	754.30	0.67	0.70	"	"	"
27	754.30	0.68		"	"	"
28	754.3	0.50		4.9	0.75	1.39
29	754.35	0.62	0.64	"	"	"
30		0.63		"	"	"
31		0.56		5.0	0.85	1.57
32	754.40	0.35	0.37	"	"	"
33		0.36		"	"	"
34		0.18	0.22	5.2	1.05	1.93
35		0.22		"	"	"

---

[1] Crystals began to separate on the sides of tube and on stem of the thermometer.

[2] Next day; melted down crystals and started again.

TABLE I—(*Continued.*)

	Barometer	Observed temp.	Temp. cor. to barom. = 755	Burette	Vol. water	Pct. water
36	754.60	0.12	0.21	5.4	1.25	2.28
37		0.17		"	"	"
38		0.18		"	"	"
39		0.22		"	"	"
40		0.12	0.19	5.6	1.45	2.64
41	754.70	0.17		"	"	"
42		0.17		"	"	"
*43		0.09	0.12	5.8	1.65	3.00
44		0.10		"	"	"

TABLE II

Started with 55.0 grams $C.Cl_3COH.H_2O$; current = 2.25 amp.

	Barometer	Temp. observed	Temp. cor. to barom. = 755	Burette	Total vol. water	Pct. water
45	748.0	1.97	2.26°	7.50	5.98	10.87[1]
*46		2.00		"	"	"
47		2.02		"	"	"
48	748.20	2.06	2.31	7.7	6.18	11.01
49		2.06		"	"	"
50		2.13	2.40	7.9	6.38	11.52[2]
51		2.15		"	"	"
52		2.25	2.50	8.2	6.68	12.21
53	748.30	2.25		"	"	" [2]
54		2.26	2.50	8.5	6.98	12.46
55		2.26		"	"	"
56		2.36	2.61	8.8	7.28	12.93
57	748.50	2.38		"	"	"
58		2.46	2.70	9.1	7.58	13.40
59		2.47		"	"	"
60		2.55	2.80	9.5	7.98	14.00[2]
61		2.56		"	"	"
*62	748.70	2.71	2.94	10.00	8.48	14.92
63		2.71		"	"	"
64		2.83	3.00	10.50	8.98	15.50
65		2.75		"	"	"
66		2.77		"	"	"
67	748.70	2.90	3.13	11.00	9.48	16.20
68		2.89		"	"	"

---

[1] Crystals separate abundantly.

[2] Melted crystals.

TABLE II—(*Continued*).

	Barometer	Temp. observed	Temp. cor. to barom. = 755	Burette	Total vol. water	Pot. water
69	748.70	2.98	3.15(?)	11.55	10.03	16.98
70		2.88		"	"	"
71		2.90		"	"	"
72		2.90		"	"	"
73		2.97	3.20	12.00	10.48	17.61[1]
74	748.70	2.98		"	"	"
75		3.07	3.30	12.50	10.98	18.30[2]
76		3.07		"	"	"
77		3.11	3.34	13.00	11.58	19.14
78		3.11		"	"	"
79	748.80	3.18	3.40	13.55	12.13	19.87
80		3.18		"	"	"
81	752.70	3.37	3.45	13.55	12.13	19.87[3]
82		3.37		"	"	"
83		3.36		"	"	"
84	752.70	3.41	3.50	14.00	12.58	20.45
85		3.42		"	"	"
86		3.45	3.52	14.50	13.08	21.07
87		3.44		"	"	"
88	752.70	3.47	3.54	15.00	13.58	21.74
89		3.45		"	"	"
*90		3.47	3.54	15.50	14.08	22.35
91		3.45		"	"	"
92		3.45	3.53	16.00	14.58	22.96
93		3.45		"	"	"
94	752.70	3.46	3.54	16.50	15.08	23.56
95		3.46		"	"	"
96		3.45	3 52	17.00	15.58	24.03
97		3.43		"	"	"
98	753.80	3.41	3.46	1.90	"	"[3]
99		3.40		"	"	"
*100		3.44	3.49	3.00	16.58	25.27[4]
101		3.50	3.54	4.00	17.58	26.40
102	753.80	3.52	3.56	5.00	18.58	27.50
103		3.54	3.58	6.00	19.58	28.54
*104		3.56	3.60	7.00	20.58	29.57

---

[1] Melted crystals.

[2] Fewer crystals.

[3] Next day.

[4] No crystals separate.

At this point the liquid was slightly colored (yellow), due partly to the reaction of the chloral hydrate on the rubber stopper. Work was stopped as soon as the color was noticed. There was also too much liquid in the apparatus to continue.

TABLE III

Made up of a solution containing 28.7 pct. water and started again.

C = 2.25 amp.

	Barometer	Observed temp.	Temp. cor. to barom. = 755	Burette	Vol. water	Pct. water
*105	750.70	3.78	3.86°		14.35	28.70
106		3.72			"	"
107		3.71			"	"
108		3.70		7.00	"	"
109	750.70	3.71	3.86	7.50	14.85	29.40
110		3.70	3.85	8.00	15.35	30.10
111		3.71	3.86	8.50	15.85	30.77
112	751.00	3.68	3.83	9.00	16.35	31.44
113		3.70	3.85	9.50	16.85	32.10
114		3.73	3.88	10.00	17.35	32.74
115		3.79	3.93	10.50	17.85	33.36
116	751.00	3.77	"	"	"	"
117		3.80	3.95	11.00	18.35	33.98
118		3.72	3.88	11.50	18.85	34.59
119		3.74	3.88	"	"	"
120		3.78	3.93	12.00	19.35	35.20
121		3.79	3.94	12.50	19.85	35.76
122		3.78	3.93	13.00	20.35	36.74
123	751.00	3.71	3.92	13.50	20.85	36.90
124		3.77	3.92	14.00	21.35	37.45
125		3.76	3.91	14.50	21.85	38.00
126		3.74	3.88	15.00	22.35	38.53
127		3.72	3.86	16.00	22.85	39.06
128		3.70	3.86	16.00	23.35	39.58
*129		3.69	3.84	16.50	23.85	40.08
130	751.00	3.68	3.83	17.00	24.35	40.58
131	751.00	3.68	3.83	17.50	24.85	41.07
132		3.67	3.82	18.00	25.35	41.56
133		3.68	3.83	18.50	25.85	42.03
134		3.67	3.82	19.00	26.35	42.50
135	751.00	3.67	3.82	20.00	27.35	43.41 [1]
136		3.67	3.82	"	"	"
137		3.67	3.82	21.00	28.35	44.29
138		3.68	3.83	22.05	29.40	45.23
139		3.69	3.84	23.00	30.35	45.99

---

[1] The liquid commenced to foam and did so until about 75 pct. water had been added.

TABLE IV

Continued with 48.5 grams of the liquid left at the end of last experiment. (45.99 pct. water); C = 2.25 amp.

	Barometer	Observed temp.	Temp. cor. to barom. = 755	Burette	Vol. water	Pct. water
140	751.20	3.70	3.85°	7.1	22.30	45.99
141		3.71	"	"	"	"
142		3.72	3.87	7.50	22.70	46.42
143		3.72	3.87	8.00	23.20	46.96
144	752.40	3.71	3.85	"	"	" [1]
145		3.76		"	"	"
146		3.76		"	"	"
147		3.76	3.85	8.50	23.7	47.50
148	752.40	3.77	3.86	9.00	24.2	48.01
149		3.77	3.86	9.50	24.7	48.52
150		3.77	3.86	10.00	25.2	49.02
151	752.40	3.78	3.87	10.50	25.70	49.52
*152		3.79	3.88	11.00	26.20	50.00
153		3.79	3.88	11.50	26.70	50.47
154		3.80	3.89	12.00	27.2	51.13
155	752.5	3.80	3.89	13.00	28.2	52.03
156		3.80	3.89	14.00	29.2	52.90
157		3.84	3.93	15.00	30.2	53.63
158		3.83	3.92	16.00	31.2	54.54
159	752.6	3.82	3.91	17.00	32.2	55.33
160		3.83	3.92	18.00	33.2	56.08
161		3.85	3.94	19.00	34.2	56.81
162		3.85	3.94	20.00	35.2	57.52

---

[1] Stood over until next day.

TABLE V

Continued 42.7 grams liquid left from last experiment (57.52 pct.).
C = 2.25 amperes.

	Barometer	Temp. observed	Temp. cor. to barom. = 755	Burette	Wt. water	Pct. water
163	752.70	3.95	4.02°	0		57.52
164		3.95	"	2.6		"
165		3.96	4.03	3.50	25.46	58.25
166		3.98	4.05	4.50	26.46	59.33
*167		3.99	4.06	5.50	27.46	60.22
168		4.00	4.07	6.50	28.46	61.07
169	752.70	4.02	4.09	7.50	29.46	61.90
170		4.03	4.09	8.50	30.46	62.67
171		4.03	4.09	9.50	31.46	63.43
172		4.05	4.11	10.50	32.46	64.15
173		4.06	4.12	12.00	33.96	65.18
174	752.60	4.06	4.13	13.50	35.46	66.16
175		4.06	4.13	"	"	66.16
176		4.08	4.15	15.50	37.46	67.37
177		4.09	4.16	17.50	39.46	68.51
178		4.09	4.16	19.50	41.46	69.56
179	752.50	4.09	4.16	21.50	43.46	70.55
180		4.10	4.17	"	"	"

TABLE VI

Continued with 35.35 grams of the liquid from last experiment.

C = 2.25 amperes.

	Barometer	Temp. observed	Temp. cor. to barom. = 755	Burette	Wt. water	Pct. water
181	752.50	4.10	4.17°			70.55
182		4.11	4.18	3.00		"
183		4.11	4.18	4.00	25.94	71.36
184	752.50	4.15	4.22	5.00	26.94	72.13
185		4.15	"	"	"	"
186		4.15	4.22	6.00	27.94	72.86
187		3.95		7.00	28.94	73.54
188		4.15		"	"	"
189	752.80	4.01	4.10	"	"	"
190		4.05		"	"	"
191		4.05		"	"	"
192		4.02	4.12	8.00	29.94	74.20
193		4.03		"	"	"
194		4.04	4.12	9.00	30.94	74.84
195		4.06		"	"	"
196	752.70	4.08	4.15	10.00	31.94	75.42
197		4.08		"	"	"
198		4.09	4.17	11.00	32.94	75.98
199		4.11		"	"	"
200		4.30	4.37	12.00	33.94	76.53
201		4.31		"	"	"
202		4.33	4.40	13.00	34.94	77.05
203		4.33	4.40	13.00	34.94	77.05[1]

---

[1] Liquid still foams, but not so badly.

Table VII

Started again with 35 grams distilled water and added from burette a solution of chloral hydrate in water (48.50 pct. chloral). Sp. gr. 1.3. C = 2.25 amperes.

	Barometer	Temp. observed	Temp. cor. to barom. = 755	Burette	Wt. chloral	Pct. water
*204	756.70	5.32	5.25°			100.0
205		5.32	"			"
206		5.33	5.26			"
207		5.33	"	7.55		"
208		5.28	5.22	7.80	0.16	99.55
209	757.00	5.29	"	"	"	"
210		5.23	5.16	8.50	0.59	98.37
211		5.19	5.12	9.00	0.92	97.50[1]
212		5.11	5.04	9.50	1.32	96.48
*213		5.09	5.00	10.50	1.85	95.20
214		5.04	4.97	11.50	2.60	93.57
*215	757.00	3.96	3.90	12.50	3.10	92.53
216		3.96	"	"	"	"
217		3.89	3.82	13.50	3.75	91.24
218		3.84	3.77	14.50	4.38	90.07
219		3.76	3.70	16.00	5.33	88.40
220		3.68	3.60	18.00	6.56	86.50
221	757.00	3.67	"	"	"	"
222		3.62	3.55	20.00	7.81	84.75
*223		3.62	"	"	"	"

---

[1] Liquid began to foam at this point and foaming increased with addition of chloral.

TABLE VIII

Started with 32.4 grams water, and added pure chloral from a burette. Sp. gr. chloral 1.51 at 20° C. C = 2.5 amperes.

	Barometer	Temp. observed	Temp. cor. to barom. = 755	Burette	Wt. chloral	Pct. water
*224	757.25	5.35	5.27°	17.55	0	100
225	"	5.36		"	0	100
226		5.33	5.22	17.75	0.302	99.08
227	757.25	5.33		"	"	"
228		5.29	5.21	18.00	0.68	97.95
229	757.25	5.29		"	"	"
230		5.24	5.17	18.20	0.98	97.06
231		5.25		"	"	"
232		5.22		"	"	"
233	757.25	5.24	5.17	18.20	"	"
234		5.25		"	"	"
235		5.25		"	"	"
236		5.22	5.14	18.40	1.283	96.19
237	757.25	5.22		"	"	"
238		5.17	5.10	18.60	1.58	95.34
239		5.17		"	"	"
240	757.20	5.10	5.02	18.90	2.04	94.60
241		5.09		"	"	"
242		5.04	4.97	19.20	2.50	92.76
243	757.10	5.04		"	"	"
244		4.96	4.89	19.50	2.90	91.77
245		4.96		"	"	"
*246		4.87	4.80	20.00	3.70	89.75
247	757.0	4.87		"	"	"
248		4.77	4.70	20.50	4.45	87.92
249		4.78		"	"	"
250		4.96	4.62	21.00	5.21	86.15
251		4.96		"	"	"
252		4.63	4.56	21.50	5.96	84.46
253	756.90	4.63		"	"	"
254		4.55	4.49	22.00	6.72	82.83
255		4.53		22.00	"	"
256	756.70	4.45	4.40	22.50	7.47	81.25
257		4.46		"	"	"
*258		4.39	4.32	23.00	8.23	79.75
259	756.50	4.35		"	"	"

TABLE IX

Started with 30 cc. water + 5 cc. pure chloral (20.11 pct. chloral), and added pure chloral from a burette. C = 2.50 amperes.

	Barometer	Temp. observed	Temp. cor. to barom. = 755	Burette	Wt. chloral	Pct. water
260	754.5	4.33		13.40	7.55	79.89
261		4.35		"	"	79.89
262		4.37	4.39°	"	"	"
263		4.37		"	"	"
264		4.37		"	"	"
265	754.70	4.26	4.28	14.40	9.06	76.81
266		4.28		"	"	"
267		4.23	4.24	14.90	9.81	75.35
268	754.80	4.24		"	"	"
269		4.22	4.23	15.40	10.57	73.95
270		4.22	"	"	"	"
271	754.80	4.19	4.20	15.90	11.31	72.60
272		4.19	4.20	15.90	11.31	72.60
273		4.19	4.20	16.40	12.08	71.29
274	754.90	4.19		"	"	"
275		4.17	4.18	16.90	12.83	70.03
276	755.0	4.18		"	"	"

Note. — Only the readings marked with a star (*) are plotted, the individual determinations falling too close together to be well represented on this scale.

ON THE EMISSION AND ABSORPTION OF WATER VAPOR BY COLLOIDAL MATTER: CORRECTION

BY P. DUHEM

The equations (7) and (8), of page 70,[1] are incorrect. In order to deduce equation (9) from equation (3), it is sufficient to note that the latter may be written

$$\begin{gathered} d\,\Big[\mathfrak{F}(v, h, \mathrm{T}) + \Pi v + (1 + h)\frac{\partial \mathfrak{F}(v, h, \mathrm{T})}{\partial h} \\ - \mathfrak{G}(\mathrm{V}, \mathrm{T}) - \Pi \mathrm{V}\Big] \\ + f(v, \mathrm{V}, h, \mathrm{T}, \Pi) \,|\, dh \,| = 0, \end{gathered}$$

and then to utilize equations (5) and the first equation (6).

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[1] This Journal, Vol. 4, February.

QUANTITATIVE LECTURE EXPERIMENTS ON ELECTRO-CHEMISTRY

BY W. LASH MILLER AND FRANK B. KENRICK

The great advances made in electro-chemistry during the last ten years — both in theory and in technical applications — have naturally caused this subject to receive more attention in universities and colleges than has hitherto been the case.

A satisfactory exposition of the principles of this essentially quantitative science, necessitates, however, the employment of quantitative lecture experiments; for the common practice of substituting tables of figures for actual measurements in the lecture room, not only produces abstruse and uninteresting lectures, but tends to obscure the experimental origin of the laws of the science. Unfortunately, the usual methods of measuring current, resistance, voltage, etc., cannot readily be adapted to the exigencies of the lecture table. The use of ordinary ammeters, voltmeters, etc., is possible only in rooms of very moderate dimensions; while the standard laboratory methods of measurement are for the most part totally unsuitable. How, for instance, could Kohlrausch's apparatus for measuring resistance be made use of, unless each student were provided with a telephone?

A number of special arrangements have consequently been devised, by Lüpke and others; these too fail in several particulars to conform to the requirements of the lecture room. In the first place, they all involve the use of a delicate galvanometer, which for demonstrations before a large audience should be aperiodic, of wide range, and big enough to be read at a distance. An instrument combining these characteristics still remains to be invented. Secondly, they are complicated by a maze of wires, cells, boxes, keys, etc., which is not only confusing to the audience, but seriously hampers the lecturer, especially if several experiments are to be performed in succession. Finally, the results of the measurements have as a rule to be extracted from the experimental data by a more or less complicated mathematical operation.

The effect of quantitative experiments carried out under such conditions is most undesirable. The attention of the students is directed so effectually to the details of the methods of measurement, that the real subject-matter of electro-chemistry — the relations between chemical composition and electrical properties — appears of but secondary importance. The writers have consequently endeavored to construct a measuring apparatus free from the defects enumerated above. The instrument, which has been continually in use during the past two years, is described in the following pages. It is provided with a dial two feet in diameter, is "dead beat," and reads directly ohms, mhos, volts, and amperes, their multiples and sub-multiples; further it can be changed from any one of these uses to any other without delay.

THE MEASURING INSTRUMENT

In carrying out measurements with the Wheatstone bridge, the resistance in one of the arms is varied until no current flows through a galvanometer. If the needle of the galvanometer incline to one side the variable resistance is too large: if to the other it is too small. In our instrument the galvanometer needle, unless exactly central, *makes an electric contact*, and thus by means of a relay, electro-magnets, etc., alters the variable resistance until the needle swings back to the central, or zero, position. A pointer moving on a dial records the change in the variable resistance, and the apparatus is so arranged that the figures on the dial give directly, in ohms, the resistance of the substance (wire, electrolyte, etc.), which is being measured.

The instrument thus performs automatically the operations which an experimenter would carry out in measuring an electrical resistance. It is also capable of making any other measurement that can be reduced to a zero method involving the alteration of *one* resistance only — for example, the determination of electromotive force, conductance, or current.

The description of the instrument falls naturally under three heads: (A) the galvanometer, with contacts; (B) the mechanical device for altering the resistance and operating the pointer; (C) the subsidiary resistance coils, and the method of altering the connections rapidly when the function of the instrument is to be changed (e. g., from voltmeter to ohm-meter.)

(*A*) *The Galvanometer*

This is constructed on the d'Arsonval model, but as it is designed to indicate merely the presence and direction (not the intensity) of a current, one of the main conditions for the efficiency of an ordinary galvanometer — constancy of the magnetic field — may be dispensed with. We have consequently employed a powerful electro-magnet in place of the usual steel magnets, thus increasing the delicacy of the instrument and ensuring good damping.

The Contacts. In our first experiments a horizontal platinum wire was attached to the frame of the coil, so that when the latter swung to the right or to the left the horizontal wire was brought into contact with one of two stationary perpendicular platinum wires; thus completing a circuit and operating the right or left relay, as the case might be. We found, however, that when contact had been made, the current apparently fused the wires together, and the galvanometer was unable to pull them apart. Three different means of overcoming this difficulty were tested. In the first place, the relay was re-wound with finer wire, in order to reduce, as far as possible, the current passing through the contacts; next, attempts were made to replace the platinum wires by infusible substances, such as carbon, or by mercury; and lastly the points of contact were moved as close as possible to the axis of the coil, in the hope that the increased leverage might be sufficient to pull the wires apart. The first change, though an obvious inprovement, was in itself insufficient to obviate all "sticking," the second resulted in uncertain electrical contact;[1] and when the perpendicular wires were moved close to the coil, the slightest vibration of the latter was sufficient to make and break the contacts in the most irregular manner.

Finally the arrangement represented in Figs. 1 and 2 was devised and found to give complete satisfaction.

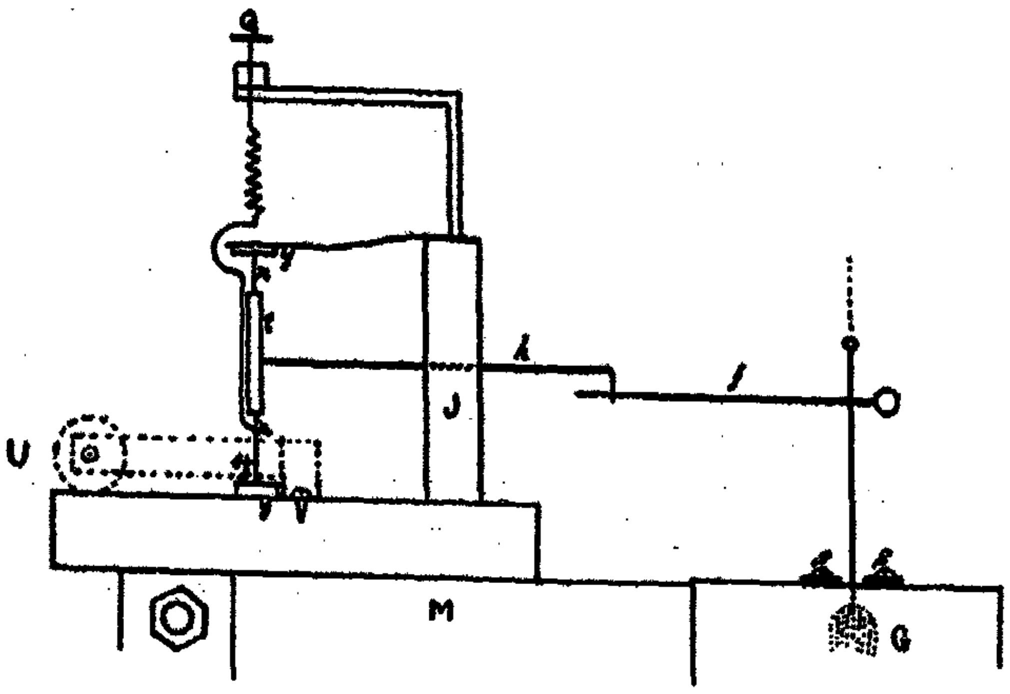

Fig. 1.

The coil G carries the glass fork *f*, which moves the glass lever *h* pivoted at *n*. Contact is made between the prolongation *e* of *h*, and *a* or *b* respectively. By this means the advantage of leverage referred to above is secured; while as the pivot *n* is held at both ends, accidental vibration of G cannot affect the contacts.

Details. The pivot is made of two needle-points *n*, fastened with sealing-wax in a glass tube *t*, to which *h* is fused. *n* communicates electrically with J, a brass frame supporting Q, by means of a spiral of fine platinum wire. The contacts *a* and *b* may be adjusted in the direction to and from the coil, by means of the wood screw and slot *w*; and in the direction to and from *h*, by the fine adjusting screws U and V. The bearings, *y*, are small pieces of window glass, in each of which, while red hot, a depression has been made with the point of a pin. They

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[1] The "cohering" effect of a wire from one pole of a small induction coil, although of some service, could not be relied upon.

are attached to J by Faraday's cement. The screw Q serves to adjust *h*. The field magnet M originally formed part of a small electric motor. The coil G is 60 mm high, 40 mm broad, formed of No. 40 silk covered copper wire wound on a soldered copper frame, and suspended by No. 44 platinum wire. The stops *s s*, prevent too wide an excursion. The relay consists of two electro-magnets with cores of iron wire, each wound with 3400 ohms of No. 36 wire. The electrical circuits are shown in Fig. 3.

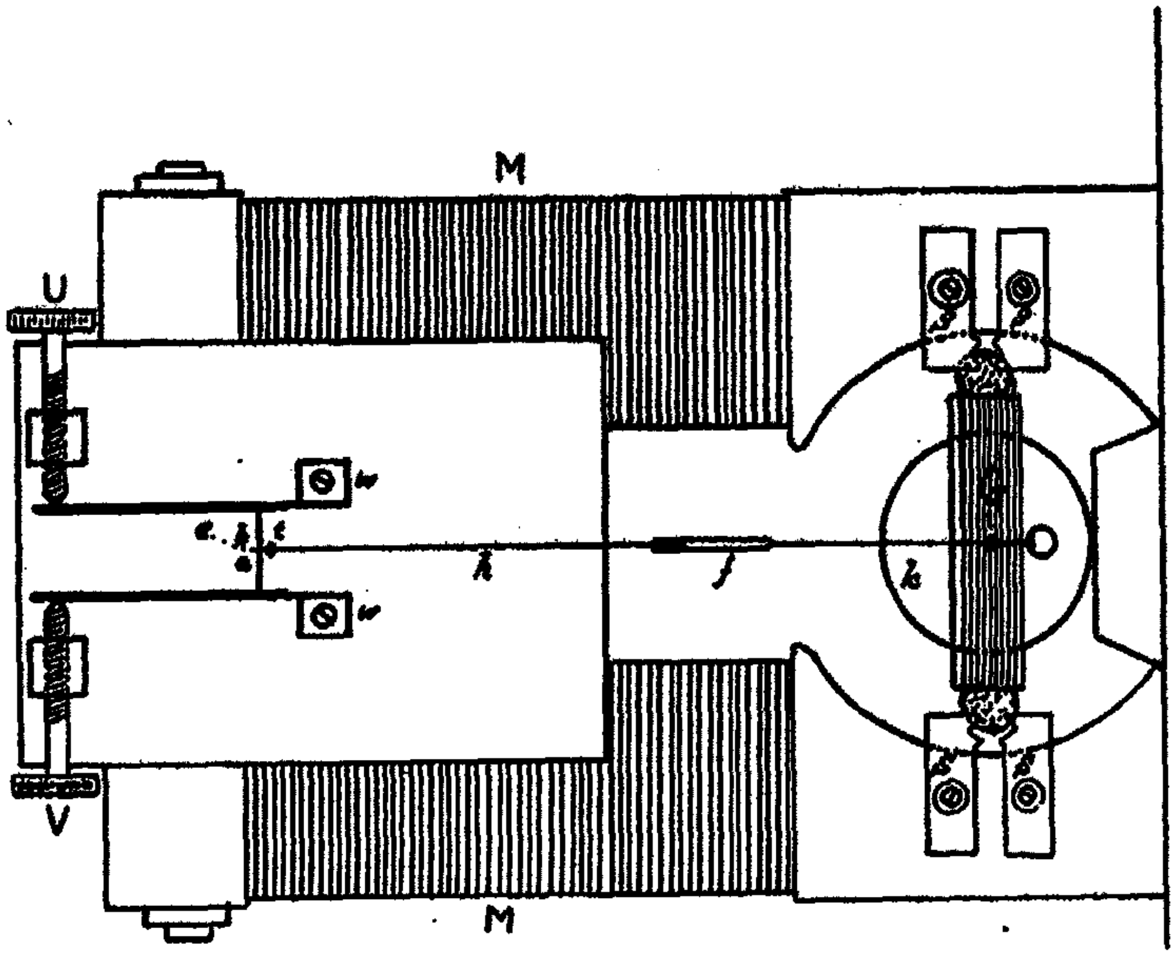

Fig. 2.

(*B*) *The Mechanical Rheostat*

The duty of this part of the apparatus (See Figs. 4 and 5) is to *increase* or *decrease* an electrical resistance, according as the galvanometer relay makes contact on the right or left side respectively. The variable resistance consists of a long wire, zigzagged on the surface of a wooden wheel, as shown in Fig. 5. S is a rubbing contact of spring brass, the "Scraper", bent so

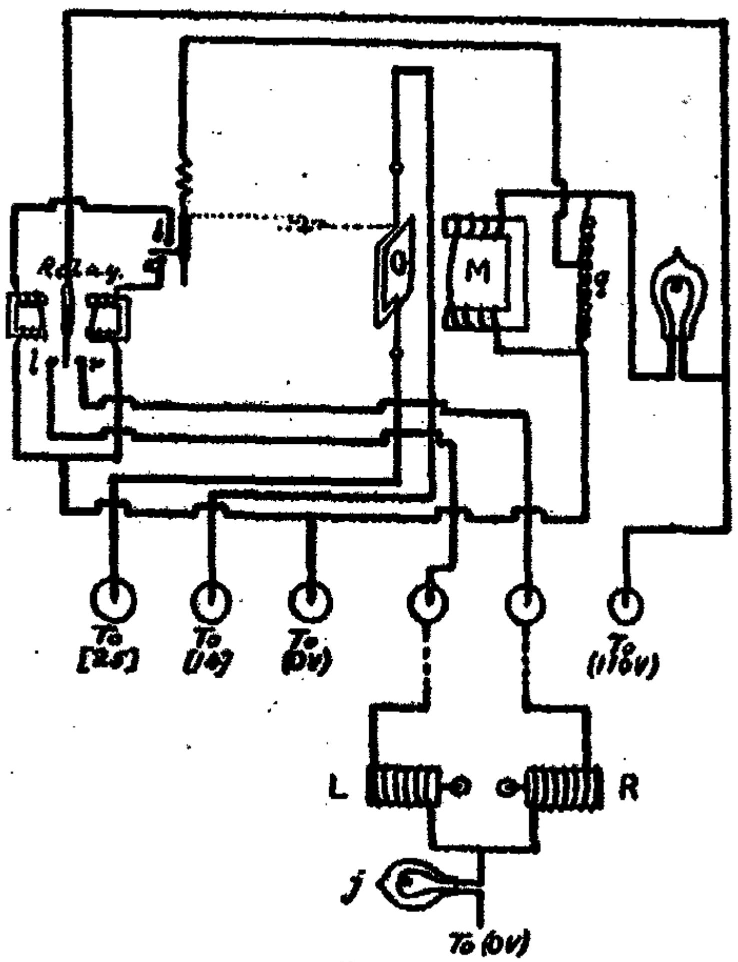

Fig. 3.

Fig 4ª

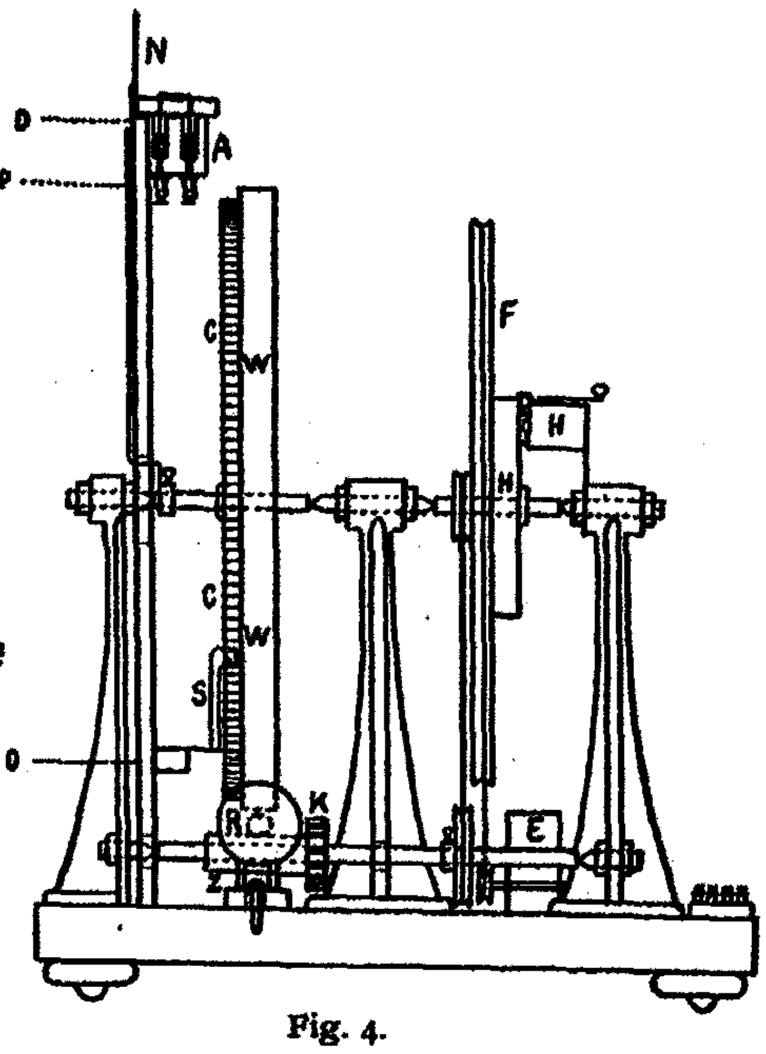

Fig. 4.

as always to touch two contact wires at once. The rollers Y and Z are kept revolving in opposite directions by the motor E and cog-wheels K. If the *right* contact of the relay be closed, a current flows through the solenoid-magnet R, which forces the wheel *d* against Z and W (as shown in Fig. 5), thus communicating the motion of Z to W, and increasing the resistance between [8] and S. The *left* solenoid, actuated by a current through the left relay, causes motion in the opposite direction and decreases the resistance. A friction block B stops the wheel promptly when the solenoid ceases to act.

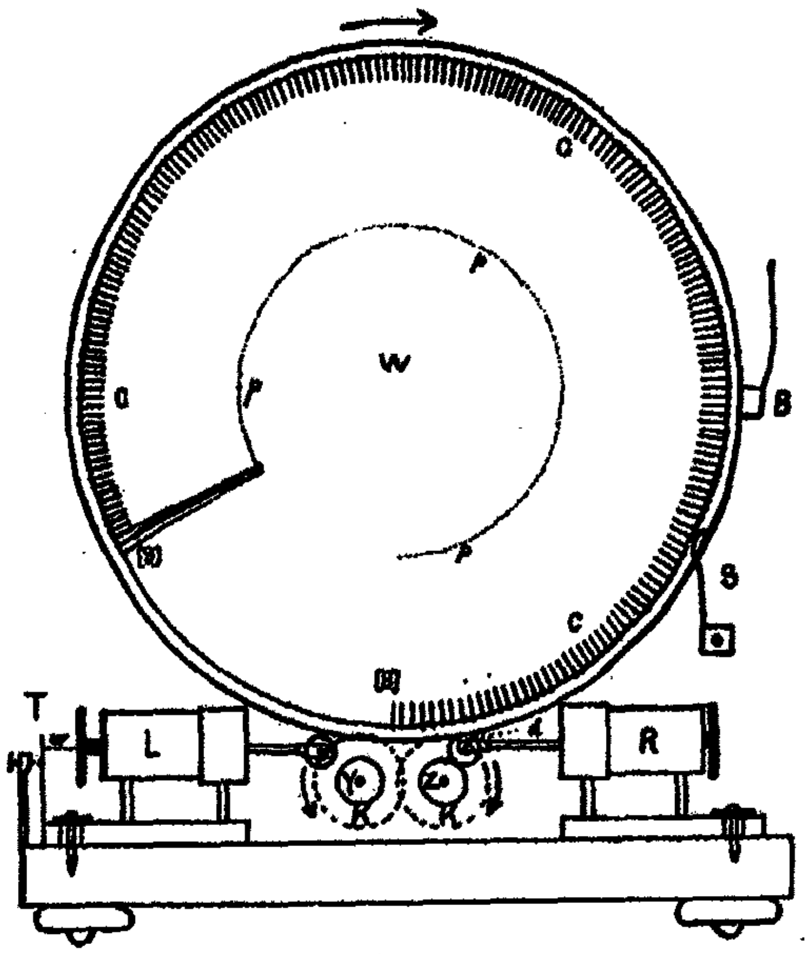

Fig. 5.

A pointer P, attached to the axis of W, moves in front of the dial D, which is divided into 100 parts. A corresponding set of numbers on the back of the wooden wheel and a small stationary pointer fixed to B indicate the readings to those behind the instrument.

F is an iron fly-wheel, used to gear down the motor and to carry the commutator H (Fig. 4). The speed of the motor can be regulated by a rheostat; a convenient rate for most purposes is about 100 revolutions of F, or 3 of W per minute.

The Resistance Wheel (W Figs. 4 and 5) is built up of three thicknesses of wood, 40 mm in all, with the grain crossed to prevent warping. 201 pieces of No. 10 copper wire bent and nicked as shown in Fig. 4*a* (C, contact wires) are fastened by small staples to the wheel; and between these and a row of pins *p*, there is stretched backwards and forwards, 135 feet of naked resistance wire. Good contact between the latter and the contact wires is ensured by soldering. The total resistance of the wire is 203.7 ohms; the resistance between two neighboring contact wires is one two-hundredth of that amount.[1]

The construction of the solenoid magnets is shown in Fig. 6. The wire (250 ohms, No. 24) is wound on a brass tube, and the whole is enclosed in a piece of two-inch iron pipe. The wheel *d* is of brass, covered with a rubber band. Each solenoid is mounted on a block of wood, whose position on the bed of the apparatus can be adjusted by a slot and wood screw. (See Fig. 5).

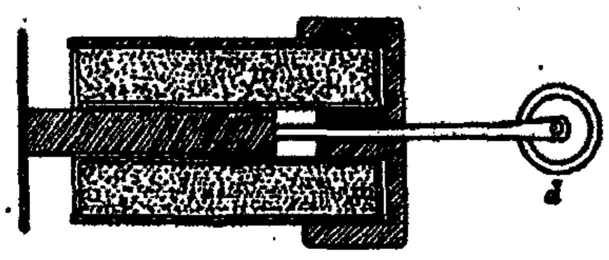

Fig. 6.

Fig. 3 shows the electrical connections. The 32-candle power lamp *j* serves as resistance and indicator.

(*C*) *The Stationary Resistance Coils*

At the back of the dial are fastened a number of coils of wire of various resistances, the ends of which communicate electrically with mercury in 32 mercury cups arranged in two rows in the wooden beam A. This takes the place of a switch-

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[1] After the apparatus had been in use for some time, it was noticed that some of the sections of wire C-*p* (Fig. 5) were slack, owing to warping; this was remedied by inserting a cord under the wires, and pushing it toward *p*. It would probably be better to make S movable and W stationary. Warping of W could then be prevented by heavy braces, and as the weight of the moving parts would be inconsiderable, weights or springs might be used as the source of power. The apparatus as described was constructed in odd hours with the material next to hand, and, although rather heavy, works very well in practice.

board. The necessary connections are made by stout copper wires (No. 10) amalgamated at the ends, and fastened in place on wooden blocks, "*Sign Blocks*", one of which seen from the back, is represented in Fig. 7.

On both sides of an upright sheet of tin attached to the sign block is written the value of one division on the dial when the connections are made; so that the very process of inserting the sign "Volts," for example, makes the connections that convert the apparatus into a voltmeter. Stops and guides prevent false connections being made, as for instance by shifting the block the width of one mercury cup to the right or left.

Fig. 7.

The construction of the *Mercury Cups* is shown in Fig. 4. An iron screw conveys the electricity from the binding post to the cup, while a small rubber washer effectually prevents any leakage of mercury.

Arrangement of the Resistance Coils

Table I gives the arrangement of the stationary resistance coils. The mercury cups are denoted by figures and letters in *square brackets*; binding posts on the bed of the machine are represented by symbols in *round brackets*; while *unbracketed numbers* give the resistance in ohms of the various coils. Dotted lines indicate electrical connections between the cups, posts, or resistance coils whose symbols they join.

TABLE I

[1]···0.1···[2]···0.9···[3]···9···[4]···90···[5]···900···[6]···9000···[7].
[8]···203.7 ohms on wheel··[9].
[10]···101.8···[*a*]···[11]···203.7···[12]···[*b*]···1833···[13]
(G)···[*c*]···[14]···1000···[*d*]···1000···[*e*]···1000···[15]···[*f*]
(*h*)···[16]···1000···[0 V.]···(*k*)

[17]···(110 V.)
[18]···(−2 V.)
[19]···(+2 V.)

[20]···Right Solenoid.
[21]···Inner Ring.
[22]···Outer Ring.
[23]···(+X).

[24]···(−X).
[25]···Scraper.
[26]···*g*, Fig. 9.

(0 V.) and (110 V.) are binding posts attached to the negative and positive of the 110 volt circuit. (+2 V.) and (−2 V.) are binding posts communicating with the positive and negative terminals of an isolated two volt circuit (storage battery). (+X) and (−X) are the terminals of the instrument, to which the electromotive force, resistance, etc., to be measured is attached. (*h*) and (*k*) are binding posts by means of which [16] and (0 V.) may be connected directly. "Inner ring," etc., refers to the Commutator, Fig. 8. (See page 611.) (G) is a binding post connected to the point marked "To [14]" in Fig. 3.

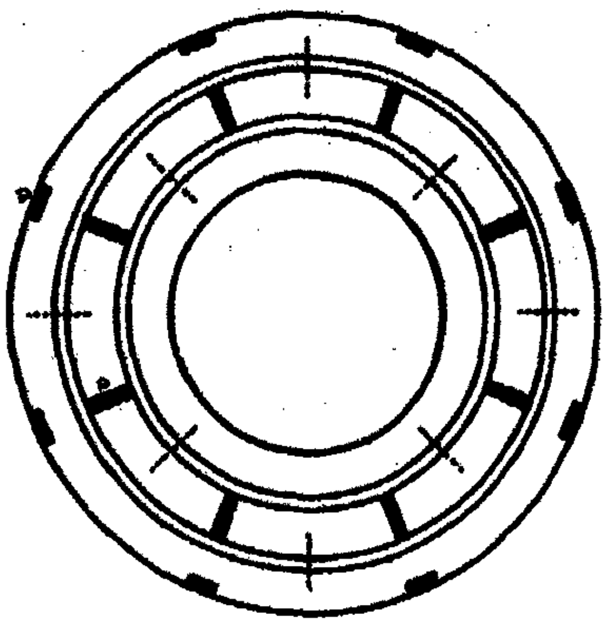


Fig. 8.

The cups [*a*] to [*f*] are situated at one end of the switchboard. If [*a*] be joined to [*b*] by a sign-block, "the Doubler", the value of one division on the dial when measuring voltage or current is doubled. When measuring ohms or mhos, the resistance in series with the galvanometer may be lessened by connecting [*f*] to [*e*], [*d*] or [*c*].

The coils 0.1, 0.9, and 10 ohms are made of heavy wire mounted on wood; the remainder, of fine silk covered "special resistance wire" wound non-inductively on glass tubes.

Connections on the Sign Blocks

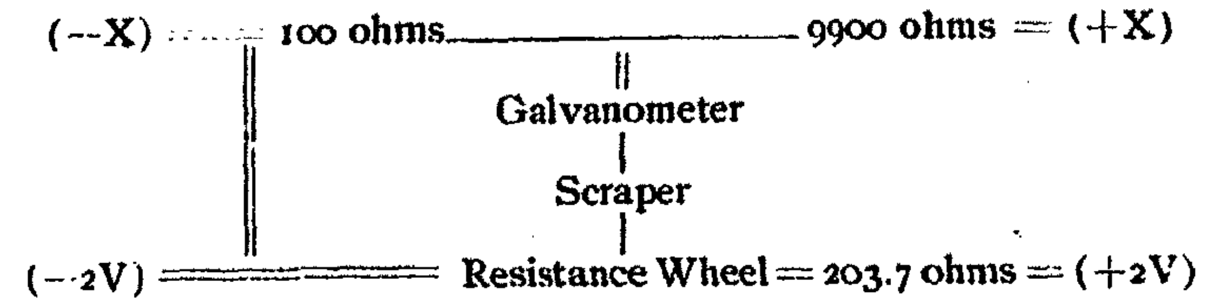
In the following table the first column gives the value of one division on the dial, the second the connections effected by the corresponding sign block.

TABLE II

1/1000 Volt	8, 11, 24; 9, 12; 10, 18; 13, 19; 14, 23.	
1/500 Volt	8, 18, 24; 9, 12; 13, 19; 14, 23.	
[1]1/100 Volt	8, 18, 24; 9, 11; 12, 19; 14, 23.	
[1]1/10 Volt	1, 8, 18, 24; 6, 14; 7, 23; 9, 11; 12, 19.	
[1] One Volt	1, 8, 18, 24; 5, 14; 7, 23; 9, 11; 12, 19.	
One+1/100 Volt	8, 11; 9, 19; 12, 18, 24; 14, 23.	
1/1000 Ampere	1, 8, 11, 24; 3, 14, 23; 9, 12; 10, 18; 13, 19.	(One ohm)[4]
1/500 Ampere	1, 8, 18, 24; 3, 14, 23; 9. 12; 13. 19.	(One ohm)[4]
[1]1/100 Ampere	1, 8, 18, 24; 3, 14, 23; 9, 11; 12, 19.	(One ohm)[4]
1/100 Ampere	1, 8. 11, 24; 2, 14, 23; 9, 12; 10, 18; 13, 19.	(1/10 ohm)[4]
[1]1/10 Ampere	1, 8, 18, 24; 2, 14, 23; 9, 11; 12, 19.	(1/10 ohm)[4]
[2]One Ohm	1, 15, 22; 5, 12, 17; 8, 16, 21; 9, 11, 25.	
10 Ohms	1, 15, 22; 7, 13, 17; 8, 16, 21; 9, 11, 25.	
[2]100 Ohms	1, 15, 22; 7, 12, 17; 8, 16, 21; 9, 11, 25.	
[3]1/100,000 Mho	1, 8, 16; 5, 15, 22; 9, 11, 25; 13, 17, 21.	
1/10,000 Mho	1, 8, 16; 4, 15. 22; 9, 11, 25; 13, 17, 21.	
[2]1/1000 Mho	1, 8, 16; 4, 15, 22; 9, 11, 25; 12, 17, 21.	
[5]1/100 Minute	17, 23; 20, 24.	

An example will make the meaning of the table clear. When the "One Volt" block is set in place the following connections are made by it: Mercury cup No. 1 with cups Nos. 8, 18, and 24; No. 5 with No. 14; No. 7 with No. 23; No. 9 with No. 11; and No. 12 with No. 19. Reference to Table I shows that these connections complete the circuit shown in the following diagram, Table III, in which the connections made by the block

TABLE III



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[1] With these blocks the "Doubler" may be used.

[2] With these blocks (*h*) and (*k*) should not be short-circuited.

[3] (*h*) and (*k*) may be short-circuited only when high resistances are being measured.

[4] The internal resistance of the ammeter.

[5] With this block in position, the instrument acts as a stop-watch. The pointer is set in motion when contact is made between the terminals (X) and stops immediately the contact is broken. The speed of the motor can be adjusted (rheostat and speed indicator) so that the pointer moves over the dial from 0 to 100 in one minute. The momentum of the fly-wheel is so great, and the friction of the resistance-wheel (W) on its bearings and on the scraper is so slight, that no appreciable change in rate is caused by bringing the solenoid into operation.

are denoted by double lines, the permanent connections by single lines. When the mechanism comes to rest, the voltage between [8] and the scraper S (Fig. 5) will evidently be one-hundredth of that between the terminals (+X and −X) of the instrument. But, as every two contact wires on the wheel (one division on the dial) correspond to one-hundredth of a volt, the dial reading gives the potential difference between the terminals in volts.

Alternative Connections

In the connections as made by the ohm and mho blocks of Table II, the resistance of the rubbing contact between scraper and wires *is added to the variable resistance* in the third arm of the Wheatstone bridge. Table IV gives a scheme of connections in which this is avoided. Our experience shows, however, that no appreciable error is introduced into the measurements by this contact, even in cases where the variable resistance amounts to but one or two ohms. There is, moreover, a drawback to the use of the blocks of Table IV: the readings on the dial do not give ohms, mhos, etc. with absolute correctness. The greatest deviation is in the center of the scale; the point 25 on the scale corresponding to 23.2 ohms, 50 to 47.6, 75 to 73.2, etc. This is partially compensated in some cases, by polarization of the electrodes when the conductance of electrolytes is measured with a direct current. With block "10^{-5} mho", for instance (for resistances of 1,000 to 100,000 ohms), the potential difference between the electrodes is in the neighborhood of 100 volts; and as the polarization with fair-sized electrodes is from two to three

TABLE IV

One Ohm	1, 15, 22; 8, 16, 21; 6, 13, 17; 9, 11.
10 Ohms	1, 15, 22; 8, 16, 21; 7, 13, 17; 9, 11.
[1] 1/100,000 Mho	1, 8, 16; 5, 15, 22; 9, 11; 13, 17, 21.
1/10,000 Mho	1, 8, 16; 4, 15, 22; 9, 11; 13, 17, 21.
[1] 1/1000 Mho	1, 8, 16; 3, 15, 22; 9, 11; 13, 17, 21.

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[1] With these blocks (*h*) and (*k*) should not be short-circuited.

volts, the conductance as measured is 2 to 3 percent less than the actual conductance. The readings obtained with the block of Table IV would consequently be nearer the truth than those with the combination of Table II.

Commutator

The most accurate results, however, may be obtained by using the blocks of Table II and alternating the current in that branch of the Wheatstone bridge which contains the electrolytic resistance. The commutator designed for this purpose is shown in Fig. 8. It is mounted on wood, and consists of three concentric brass rings, one of which is divided into eight isolated sections (+ and —) by small blocks of vulcanite, *v*. A pair of brushes set the inner and outer rings respectively in communication with mercury cups [21] and [22]; and two brushes on the center ring, one behind the other at an interval of one section, communicate with the electrolytic resistance. As the commutator revolves, the direct current to and from the mercury cups is interrupted; while in the circuit containing the electrolyte it is transformed into a series of pulsations in opposite directions.

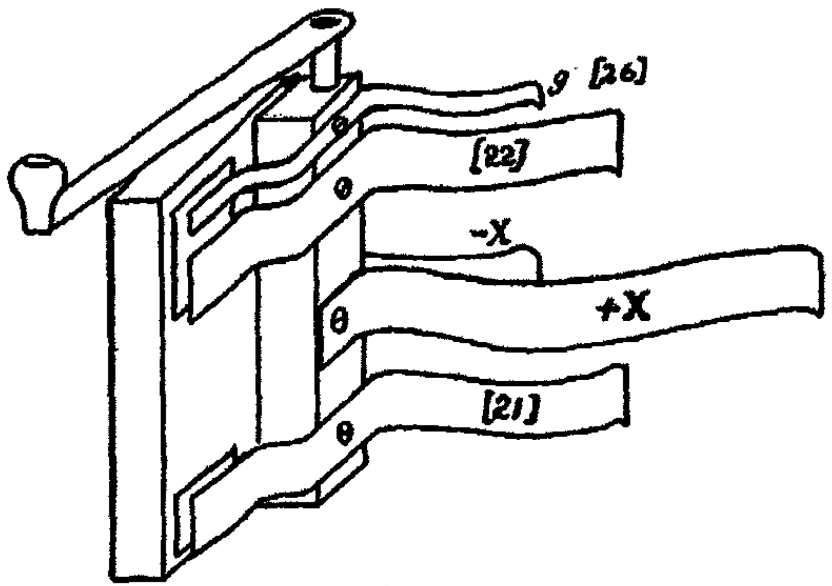

Fig. 9.

In order to prevent these interruptions from affecting the galvanometer, connection with the latter is broken at the right moments by small pieces of vulcanite, *v*, let into the margin of the outer ring.

All five brushes are mounted on a hinged frame (Fig. 9);

when thrown back so as not to touch the commutator rings, they make permanent connections between [21] and [23], [22] and [24], [26] and the galvanometer coil (G).

QUANTITATIVE LECTURE EXPERIMENTS IN ELECTRO-CHEMISTRY

With the aid of the instrument just described, it is an easy matter to illustrate a course of lectures on electro-chemistry by a series of quantitative experiments. All the apparatus, etc., described in the following paragraphs has stood the test of actual use in the lecture room, most of it having been employed in the lectures on elementary physical chemistry during the winters 1898–1899, and 1899–1900.

Electrolysis

(*I*). *Electrolysis, Current, Resistance.*—Two of the common (Hofmann's) electrolysis apparatus may be set up in series with a 32-c. p. incandescent lamp, the first being filled with maximum conducting sulphuric acid (one vol. acid to five vols. water) and the second with a mixture of one vol. acid and forty vols. water. If the terminals be connected to the positive and negative of the 110 volt circuit, the potential difference between the electrodes of the first cell will be found to be about 10 volts, and of the second about 22 volts. But although resistance, voltage, and concentration are thus different in the two cells, and current alone is the same in both, the volume of hydrogen liberated in the first cell is the same as that in the second.

(II). *Electro-chemical Equivalents.*—The following cells are arranged in series, and the terminals connected to the 110 volt (better 220 volt) circuit.

(*a*) Apparatus, Fig. 10, filled with sodium chloride sol'n. — 70 cc sat. sol'n. and 30 cc water.

(*b*) Apparatus, Fig. 10, filled with nitre sol'n. — Nitre one part, water five parts.

(*c*) Hofmann's electrolysis apparatus, filled with max. conducting sulphuric acid.

When about 10 cc hydrogen have been liberated, the current is stopped, the central pinch-cocks are closed, and the solutions from the cathodes are run out and neutralized with 1/50 normal acid. If two burettes be used, clamped close together, it will be apparent that the amount of acid needed is the same in each case. By adding a *little* litmus to the acid in the burettes, the column of liquid may be made more visible. Finally, the amount of alkali equivalent to the hydrogen liberated may be calculated.

(III). *Faraday's Constant.* — The determination of this constant may be effected by electrolyzing sulfuric acid solution and measuring time, current, and amount of gas evolved. In order to obtain a large volume of gas in a short time the decomposition is carried out under reduced pressure. For this purpose the cell shown in Fig. 11 may be employed. The apparatus is filled with maximum conducting sulfuric acid, which had been boiled to expel air, and a column of mercury is drawn up into the graduated tube by connecting *z* to a filter-pump. The electrical connections are so arranged that inserting a plug closes the following circuits:

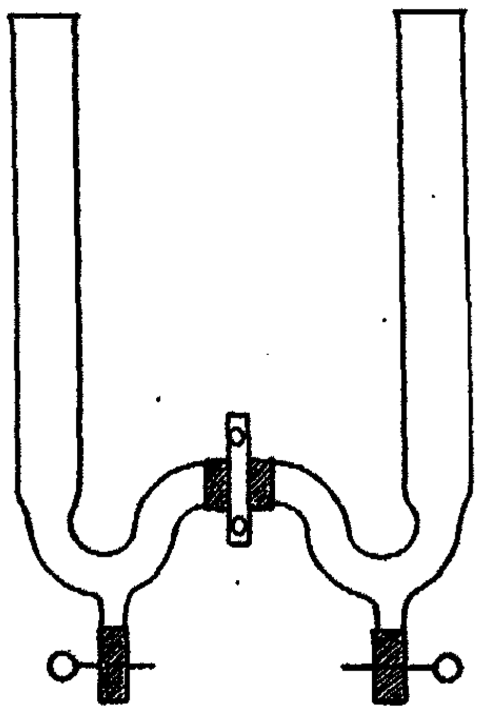

Fig. 10.

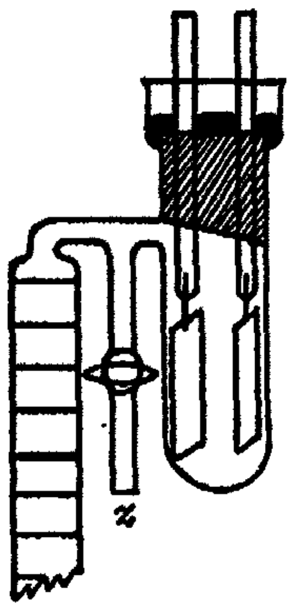

Fig. 11.

(*a*) Positive of 110 volt circuit, — 16 c. p. lamp, — cell Fig. 11, filled with max. cond. sulfuric acid — negative of 110 volt circuit.

(*b*) Terminals of measuring apparatus, with block "1/100 minutes."

When about 10–15 cc gas have been collected (half a minute or so), the plug is withdrawn, and the temperature, pressure, volume of gas, and duration of electrolysis, are noted. Next the block "1/100 ampere" is inserted in the measuring instrument, and the current determined under the same conditions as before

Conductivity

(IV). *Ohm's Law for Electrolytes.*—If a 1.5 pct copper sulfate solution be electrolyzed between copper plates (3 in. by 6 in.) 1½ inches apart, in series with a rheostat, measurements of the voltage at the electrodes, and of the current passing through the cell, for different amounts of resistance in the rheostat, show that these quantities are proportional to each other. (Use 1/100 volt and 1/100 ampere blocks). The necessary changes in the connections may be made conveniently by means of a "3-pole double-throw switch", or a substitute constructed of wire and mercury cups.

(V). *Conductance and Dimensions of Cell.* — That the conductance varies inversely as the distance between the electrodes, may be shown by filling a one-liter graduated cylinder (70 mm diameter) with copper sulphate solution (one gram of blue vitriol crystals in the liter) and measuring the conductance (10^{-4} mho block) between two circular copper plates, at various distances apart. As "measuring cylinders" are usually *not* cylindrical near the bottom, it is better to fix the lower plate at about the 200 cc mark. A piece of stout copper wire soldered to each plate and covered loosely with glass tubing, serves as a handle, and at the same time establishes electrical communication.

The relation between conductance and area of conductor, may be shown with the cell represented in Fig. 12. If the electrolyte be allowed to escape through the tube *a*, it will be found that the conductance decreases, and that it is proportional to the height of the meniscus.

(VI). *Conductance and Temperature.*—By using the "10 ohms" block, and connecting (*h*) and (*k*) through a rheostat, the resistance of a 16 c. p. lamp may be determined at temperatures from full white heat down to blackness. The extreme ratio is about 3 : 5.

Electrolytes may be measured, using "dip-electrodes", in a beaker; or if the conductance is too great, in a U-tube warmed in a beaker of water. The contrast between the temperature coefficient of dilute sulphuric acid and that of 10 pct phosphoric acid is very marked.

(VII). *Conductance and Concentration — Ostwald's Law.*— By using the cell represented in Fig. 12 the molecular conductivities of solutions of various concentrations (or numbers proportional to these) may be read directly on the dial of the measuring apparatus. The cell is made of glass and wood, the joints being kept tight by a piece of rubber tubing compressed by the wood screws as shown. The dimensions are: one centimeter through, 10 cm wide, and 50 cm high. Platinum foil fastened to strips of glass (1 cm x 50 cm) by Faraday's cement serves as electrodes (*b b*, Fig. 12).

If 25 cc 1/250-normal hydrochloric acid be introduced through a funnel, and the electrodes be connected to the binding posts of the measuring apparatus (10^{-5} mho block) the pointer will indicate the molecular conductivity in mhos directly.[1] Addition of water causes no alteration in the reading. (Stirring may be effected by blowing through a glass tube.) If, on the other hand, 25 cc of normal acetic acid be taken, and the volume be increased by successive additions of water from 25 to 50, 100, 200, and 400 cc, it will be found that the conductance is proportional to the square root of the volume; the conductance for volume 400 cc for instance, is double of that for 100 cc. and that again double the conductance of the 25 cc originally taken.

(VIII). *Isohydric Solutions.*—To prepare (approximately) "isohydric" solutions of acetic and hydrochloric acids, add water

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[1] When working with small volumes (25 cc), the current should be shut off as soon as the measurement is completed: otherwise the temperature of the electrolyte is apt to rise.

to 25 cc normal acetic acid in the cell (Fig. 12), until the conductance is equal to that of 25 cc 1/250-normal hydrochloric acid in the same apparatus. Then add water to the hydrochloric acid until its volume is the same as that of the acetic acid.

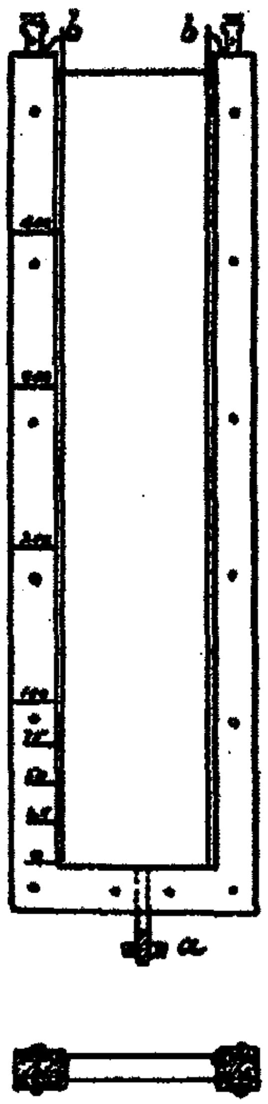

Fig. 12.

If these two acids be mixed in the cell, the conductance of the mixture is the sum of those of the acids separately; if more concentrated acids be mixed, the sum is less; if more dilute, greater. The differences are well marked, and in accordance with the calculations.

(IX). *The Solubility of Lead Sulphate, etc.*—may readily be calculated from measurements of the resistance of a saturated solution, using "dip electrodes".

Electromotive Force

As the least current that will operate the galvanometer contact is about 10^{-5} ampere, the internal resistance of the cells whose electromotive force it is desired to measure must be low. Siphons, capillaries, and cotton-wick connections are consequently inadmissible. The following forms have given satisfaction.

(X). "*Calomel Cell*".—A glass tripod such as are used in exsiccators, but with legs only 2 cm long, stands in a crystallizing dish and supports a circular sheet of amalgamated zinc 10 cm in diameter. The bottom of the dish is covered with mercury, and a solution of zinc chloride mixed with calomel is poured in. Connection is made with the mercury by platinum wire sealed through a glass tube which is fastened by a split cork to the edge of the crystallizing dish. Two of these cells, with solutions of different strengths, may be connected zinc to zinc, and the resultant electromotive force measured directly in 1/1000 volts.

(XI). *Amalgam Cells.*—The amalgams (1 pct and 1/100 pct zinc amalgam) are contained in small crucibles standing in a crystallizing dish filled with the electrolyte (10 pct zinc sulphate).

(XII). *Diaphragm Cells.* — Small "porous pots" of unglazed porcelain standing in beakers are useful when strong acids are to be used; they are, however, difficult to clean, especially if precipitates have been formed in the walls. A most satisfactory cell may be made from the lower half of a thick glass bottle (one pound potash bottle) by splitting it longitudinally with a hot iron. A piece of parchment paper is laid between the two halves, and the whole bound together with rubber bands. The edges of the glass need not to be ground smooth. This apparatus serves for concentration cells (normal and 1/100-normal silver nitrate, with silver electrodes), precipitation cells (silver nitrate on both sides of the diaphragm, sodium chloride in addition on one side) and cells with complex salts (silver nitrate, and silver nitrate with potassium cyanide). When the diaphragm gets dirty, it can quickly be replaced by a fresh piece of paper.[1]

Polarization

(XIII). *Constant and Inconstant Cells.* — If a Grove's cell of the ordinary form be short-circuited through the measuring apparatus (1/100 ampere block, introducing one ohm into the circuit), the current falls off but 1/100 ampere in a minute. If, on the other hand, the nitric acid in the porous cell be replaced by zinc sulphate, the fall in current amounts to 1/10 ampere in the same time.

(XIV). *Polarization by Current.* — If after measuring the conductance of hydrochloric acid solution in the cell of Fig. 12, with *direct current*, the 10^{-5} mho block be quickly replaced by the 1/100 volt block, the polarization may be measured and its gradual disappearance noted. The effect of short-circuiting the cell, or of reversing the current through it, may also be shown.

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[1] For cells whose E. M. F. lies between one and two volts, use the 1/100 volt block with doubler; or the block 1 + 1/100 volt (range fron one to two volts in 1/100 volts). With cells of high resistance the latter cannot be employed.

(XV). "*Maximum*" *Electromotive Force of Polarization.*—Two platinum wires connected with the terminals of the measuring apparatus (1/100 volt block with doubler) are dipped just below the surface of a solution of silver nitrate (lead acetate, etc.). As the resistance wheel is turned in the direction of the arrow in Fig. 5 the potential difference between the two platinum wires increases until at last a current of 10^{-5} ampere flows through the electrolyte, and the left galvanometer contact is made. In order that the instrument may automatically indicate this "maximum electromotive force of polarization" the left solenoid is attached by the cord *w* (Fig. 5) to the contact T, which when closed, completes the circuit operating the right solenoid. By replacing one of the wires by foil, the polarization at the anode and at the cathode may be measured separately.

The Chemical Laboratory of the University of Toronto,
July, 1900

NEW BOOKS

Sur l'Equilibre des Systèmes chimiques. *By Paul Saurel. Thèse (Bordeaux), 1900. Tours: Deslis Frères.*—In this Doctor's dissertation, the author has undertaken to present the thermodynamic theory of chemical equilibrium in a compact and simple manner; and at the same time to fill certain obvious gaps in the theory as it at present stands. After an introductory chapter on the fundamental principles of thermodynamics, he gives a short derivation of the phase rule, developed from that given in this Journal, 3, 137. The third chapter is an elegant and complete discussion of the theory of 'indifferent points,' in bivariant and trivariant systems and in the general case, originally outlined in this Journal, 4, 193. In the fourth chapter, on Various Theorems, the theorem of Maxwell (Cf. 3, 214) is developed for the general case; the equations of Riecke are derived, i. e., the zero-determinants of the $dp/d\theta$'s, m's, v's, and of the $dp/d\theta$'s, m's, η's, for systems of phases in equilibrium; and a discussion is given of the theorem of van der Waals, relating to the pitches of boundary curves. The concluding chapter, on the Displacement of Equilibrium, develops Planck's form,

$$dp \cdot \delta v - d\theta \cdot \delta\eta + \Sigma\Sigma\Sigma \frac{\partial\mu}{\partial m} dm\delta m = 0,$$

of the equations of equilibrium; and derives systematically from it the displacement theorems of Clapeyron, Gibbs, Konowalow, Le Chatelier, van't Hoff, Robin, and Moutier. The latter part of this work has been published in this Journal, 3, 548; the former more extensive part may be expected to appear later in the same place. *J. E. Trevor*

Théorie générale des Dissolutions. *By J. J. van Laar. Reprinted from Archives Teyler (2) 6. 18 × 28 cm; 64 pp. Haarlem. Loosjes.*—This brochure presents a general exposition of the theory of solutions, under the assumptions that the solvent is partially associated and the solute partially ionized. It begins with an account of the criteria of equilibrium, and of Planck's form of Gibbs's energy equation; and then passes to Planck's resolution of the entropy, the 'paradox of Gibbs', a determination of the form of the fundamental function $\Psi = \eta - (E + pv)/\theta$ and of the derivatives $\psi = \partial\Psi/\partial n$, and the general properties of the functions ψ and of their derivatives. Next comes a formulation of the ionization and dissociation equilibria in a solution, and chapters on osmotic pressure and heats of dilution. The work is concluded by the theory of the equilibrium of a number of special systems: solution and solid solute, solution and gaseous solute, two liquid layers, solution and solid solvent, solution and gaseous solvent, the formulas of Kirchhoff. The treatment is a thorough-going specimen of this kind of special theory. *J. E. Trevor*

Recherches sur les Gaz. *Volumes moléculaires et états correspondants. By A. Leduc. 14 × 23 cm; pp. 116. Paris: Gauthier-Villars et Fils, 1898. Price: paper, 2.50 francs.*

Nouvelles Recherches sur les Gaz. *Applications. By A. Leduc. 14 × 23 cm; pp. 54. Paris: Gauthier-Villars et Fils, 1899. Price: paper, 1.50 francs.*
In these two brochures, Leduc gives a connected account of his recent work on the molecular volumes of gases. After a historical introduction, the topics considered in the first are, successively, the composition of air, the density of gases, critical temperatures and pressures, combining weights, compressibility, the 'law of molecular volumes', molecular volume and density, coefficients of expansion, and mixtures of gases. In the second, he treats vapor-density and specific volume, saturated vapors, abnormal vapors, dissociation and polymerization, specific heats, and irreversible expansion. *J. E. Trevor*

Chemistry an exact Mechanical Philosophy. *By Fred. G. Edwards. 14 × 22 cm; pp. xii + 100. London: J. and A. Churchill, 1900.* — "The object of this work is to determine the exact shape of the atoms, to find their relative positions in space, and to show that chemical force is purely a function of matter and motion. The shapes obtained for the different atoms is the subject-matter of a British patent dated 1897. The exact agreement in the following points should convince the most skeptical of the truth of this discovery: (1.) The recurring shapes of the atomic models agree with the periodicity of the elements; (2.) Twelve inverse pyramidal faces predominate just so far as the particular atom is acidic in characteristics; (3.) Projecting pyramidal faces predominate just so far as the particular atom is metallic in characteristics; (4.) The sudden change from acidic to metallic models at the points between chlorine and potassium, bromine and rubidium, iodine and caesium respectively; (5.) The formation of the basic and acidic oxides; (6.) The absolutely perfect relationship of the atomic shapes of the organic elements; and the hypothetical bonds of the same representative elements, carbon, nitrogen, oxygen, and hydrogen, mechanically accounted for; (7.) The formation of such complicated molécules as aurin or tri phenyl-methane with every bond mechanically accounted for. ... The conclusions herein deduced will form a fitting climax to the discoveries of a century which has produced the atomic theory of Dalton, the theory of heat as a mode of motion, and the discoveries of the correlation of physical forces, and that force like matter is indestructible."

Leerboek der anorganische Chemie. *By A. F. Holleman. 16 × 24 cm; pp. iv + 467. Groningen: J. B. Wolters, 1898. Price: 8 florins (Dutch).*

Lehrbuch der anorganischen Chemie. *By A. F. Holleman. In Gemeinschaft mit dem Verfasser bearbeitet und herausgegeben, von Wilhelm Manchot. 15 × 22 cm; pp. xii + 439. Leipzig: Veit and Co., 1900. Price: bound, 10 marks.*

Descriptive General Chemistry. *A Textbook for Short Course. By S. E. Tillman. Second edition. 15 × 23 cm; pp. x + 429. New York: John Wiley and Sons, 1899. (London: Chapman and Hall, Limited.) Price: cloth, $3.00 (12/6) net.*

Einführung in die Chemie, *in leichtfasslicher Form. By Dr. Lassar-Cohn. 13 × 21 cm; pp. xi + 229. Hamburg und Leipzig: Leopold Voss, 1899. Price: paper, 4 marks.*

Inorganic Chemistry for Advanced Students. *By Henry Roscoe and Arthur Harden. 12 × 17 cm; pp. viii + 432. New York: The Macmillan Company, 1899.*

Chemistry for Organized Schools of Science. *By S. Parrish. With Introduction by D. Forsyth. 12 × 17 cm; pp. vii + 262. New York: The Macmillan Company, 1899.*

Elementary Chemistry. *By Albert L. Arey. 12 × 19 cm; pp. viii + 271. New York: The Macmillan Company, 1899. Price: cloth, $0.90.*

Elementary Studies in Chemistry. *By Joseph Torrey, Jr. 13 × 19 cm; pp. viii + 487. New York: Henry Holt and Co., 1899.*

Leitfaden für den Unterricht in der anorganischen Chemie. *By Joachim Sperber. Part I. 16 × 24 cm; pp. 120. Zürich: E. Speidel, 1899. Price: paper, 3 marks.*

Inorganic Preparations. *By Felix Lengfeld. 12 × 18 cm; pp. ix + 55. New York: Macmillan and Co., 1899.*

Laboratory Manual: *Experiments to Illustrate the Elementary Principles of Chemistry. By H. W. Hillyer. 15 × 23 cm; pp. vi + 200. New York: The Macmillan Company, 1899. Price: cloth, $0.90.*

Chemical Experiments. *By John F. Woodhull and M. B. Van Arsdale. 13 × 19 cm; pp. 136. New York: Henry Holt and Company, 1899.*

Perhaps the most pretentious of the above textbooks on introductory general chemistry is that by the well-known Dutch chemist, Professor Holleman. It is an attempt to combine the elements of physical chemistry with the usual descriptive matter. After an introduction on chemical phenomena and operations, and the chemical elements, the author begins with oxygen, hydrogen, and water, and passes immediately to the laws of combination and the atomic hypothesis. Chlorin and hydrochloric acid lead to a general consideration of acids, bases, and salts; and then, after ozone and hydrogen peroxide, osmotic pressure and molecular changes of freezing and boiling temperatures follow. The halogens furnish a transition to the theory of electrolytic dissociation; and sulphur to the phase rule. Then, after selenium and tellurium, thermochemistry and thermodynamics are considered. The treatment of thermodynamics is too superficial to be intelligible. The nitrogen and carbon groups introduce specific heat and isomorphism, and the periodic system; the alkali metals lead to solubility curves, heats of neutralization, hydrolysis, and the theory of indicators; then a number of metals lead to Nernst's theory of electromotive forces; and the remaining metals complete the book. Due attention is given throughout to important technical processes.

Obvious objections to all this are that the theoretical matters are, for the most part, introduced too early; that the phase rule is applied only to a one-component system, sulphur; and that mathematical relations are often introduced without any attempt to outline their derivation. The descriptive chemistry makes an agreeable impression; and it has been kept within reasonable bounds. The German version is a free translation, somewhat altered in details by both the author and the translator. It is exceedingly well gotten up.

Prof. Tillman's treatise is designed to meet the requirements of the instruction at the United States Military Academy; where so little time is devoted to chemistry that systematic laboratory instruction is not given. The six chapters of the book treat in order: essential principles, affinity, non-metals, metals, organic chemistry, and applied chemistry. Only the first two chapters treat theory; but they give a heavy dose of it. The first gives the regulation theory of the usual introductory treatise; while the second goes into the newer ideas of mass-action, dissociation, solution theory, thermochemistry, and the periodic law. The whole is immensely compact, and is doubtless well adapted to its purpose.

Lassar-Cohn's *Einführung in die Chemie* is the embodiment of a course of university extension lectures. It begins with water and hydrogen; and passes through the halogens to the laws of combination and the atomic and molecular hypotheses. The non-metals come next, and a half dozen metals conclude the whole. The book has the simple style and clearness of statement that distinguishes its author's recent popular book on applied chemistry.

A book of different scope is Roscoe and Harden's *Inorganic Chemistry for Advanced Students*; for it is intended to supplement a brief beginner's book — Roscoe and Lunt's *Chemistry for Beginners*. Presupposing, accordingly, the more elementary matters, it proceeds to a pretty thorough development of systematic inorganic chemistry. The arrangement is good; and brief chapters on solubility, thermochemistry, electrochemistry, and the determination of molecular weights in solutions, are interspersed at suitable points.

A small book for beginners is Parrish's *Chemistry for Organized Schools of Science*. It gives a treatment of limited scope, to accompany a course of laboratory experiments. Hydrogen, oxygen, carbon, nitrogen, the halogens, sodium, and sulphur are taken up.

A schoolbook that covers the usual matter of an outline introductory course is Arey's *Elementary Chemistry*. It is the author's idea "To omit all reference to those properties of the substances studied in the laboratory which can be learned by observation of the substances themselves; but to render the work more complete than it would otherwise be by stating such properties as cannot be shown by experiments adapted to secondary schools." This throws wholly upon the teacher much of the work that the book might do; and so limits its usefulness to the case of a competent teacher with small classes. The attitude of the book toward the more important theoretical matters is dogmatic.

In Torrey's *Elementary Studies in Chemistry*, great care is taken to explain everything that is introduced. Extensive laboratory instruction is called for. The treatment includes: measurement of volumes and temperatures; vapor-pressure and vaporization; hydrogen, oxygen, and water; the molecular theory, oxidation, chemical equations, and the determination of combining weights; acids, bases, salts, and ionization; and descriptive inorganic chemistry, beginning with the alkali metals and ending with the elements of the fourth group. The first thirty Lectures are unprovided with titles, and the book has no index.

The last of our list of textbooks, Sperber's *Leitfaden*, is the first third of an illustrated series of notes on a course of classroom and laboratory instruction. The author promises a new edition in more finished form, if the present one proves successful. The descriptive parts of the treatment are the best.

Three laboratory manuals remain for comment. Prof. Lengfeld's *Inorganic Preparations* is a serious book. It gives an extensive selection of typical preparations, and refers the student in each case to the original literature. The preparations are arranged in the order of increasing difficulty, and they introduce all processes in general use. Such a course as this will form a very important feature of the training of a scientific chemist. Prof. Hillyer's book is a thoroughly good manual for laboratory instruction in connection with an introductory lecture and textbook course. The selection of experiments is good, the practical directions are good, and an admirable feature is the collection of quantitative experiments to illustrate theoretical points of fundamental importance. The book is probably one of the best of its kind. Woodhull and Van Arsdale's *Chemical Experiments* is a well chosen and well arranged series of simple laboratory experiments for schools. Accompanied by a good textbook, it should give good results, even in the hands of a mediocre teacher. The scope of the book is limited, embracing oxygen, definite proportions, hydrogen, chlorine, acids, bases, salts, sulfur, nitrogen, carbon, fermentation, and potash.

J. E. Trevor

The Grammar of Science. *By Karl Pearson. 14 × 22 cm; pp. xviii + 548. (A. and C. Black). New York: The Macmillan Company, 1900. Price: cloth, $2.50.* — One of the most interesting and important phases of the current development of scientific thinking is the intelligent attention being given alike by professional philosophers and representatives of the special sciences to the questions of scientific epistemology. It is becoming very generally realized that knowledge is a construction on the part of the mind, that the world is made up of bodies and that bodies are complexes of sense-perceptions, that ultimately reality is a phantom—not an object of scientific investigation. Men who have done much to develop this view, and to apply it in making physical science sound and clear, are Helmholtz, Mach, Hertz, Stallo, and Karl Pearson. One of the most widely read books on the general subject is Pearson's *Grammar of Science*, which first appeared in 1892, and is now out in a revised and enlarged edition. Pearson's aim is to ally idealism and scientific philosophy; and one can say at least of his work that it is suggestive and inciting. It is certainly a book to be reckoned with, even though it requires to be read with the eyes open. The new edition differs from the old chiefly in the addition of chapters giving an outline of the author's work on the quantitative aspect of evolution. This, however, is a matter of special interest, despite its undoubted value: it is a matter for the biologist, and not for the physicist. An admirable feature of the work is the printing of summaries at the close of the several chapters.

J. E. Trevor

La Mathématique. Philosophie; Enseignement. *By C. A. Laisant. 14 × 22 cm; 292 pp. Paris: Georges Carré et C. Naud, 1898.* — M. Laisant's essay is a most entertaining *causerie* on the philosophy of mathematics. It is neither a learned dissertation nor a popular article, but a simple discussion for the general reader who has an intelligent interest in elementary mathematics. Its three parts consider successively the philosophy of pure mathematics, the philosophy of applied mathematics, and mathematical instruction. The first two of them constitute a broad, general survey of the present state of mathematical research; and the one on instruction insists that if the really essential elements of arithmetic, geometry, algebra, analytics, and calculus were taught in the schools, free from the mass of subsidiary details in which they are always enveloped, it would be possible to impart a sound idea of them all in the time now required to teach as separate branches the first three. This last is so obvious a contention that it would not seem worth stating, were it not that it is never acted upon in secondary instruction. Surely, to teach mathematic instead of mathematics would immensely increase the efficiency of our schools.

M. Laisant writes a delightful French style; and he excuses his simplicity in the words: "At a time when we see so many learned dissertations on unimportant or futile subjects, why may not one's pen be allowed to run a little on a serious subject; if only in order to reestablish equilibrium." *J. E. Trevor*

Discourse on Method. *By René Descartes, (1596-1650). Translated by John Veitch. 13 × 19 cm; pp. vi + 87. Chicago: The Open Court Publishing Co. Price: paper, 25 cents.* — We take pleasure in announcing the appearance of a neat and inexpensive English edition of Descartes's famous *Discourse on the Method of Rightly Conducting the Reason, and Seeking Truth in the Sciences.* The text is translated from the French, and collated with the Latin, by Dr. John Veitch, of the University of Glasgow. Men of science as well as men of philosophy will welcome this convenient form of an important classic of scientific philosophy. *J. E. Trevor*

The Evolution of General Ideas. *By Th. Ribot. Translated from the French by Frances A. Welby. 14 × 20 cm; pp. xi + 231. Chicago: The Open Court Publishing Company. Price: cloth, $1.25.* — The author states the aim of this work to be a study of the development of the mind as it abstracts and generalizes; and to show that these operations exhibit a perfect evolution: that they exist already in perception, and advance by successive stages to the more elevated forms of pure symbolism. He accordingly seeks to establish three main periods in the operations: (1.) inferior abstraction, independent of words; (2.) intermediate abstraction, accompanied by words, which gradually increase in importance; (3.) superior abstraction, where words alone exist in consciousness and correspond to a complete substitution. The book is the first of a series designed to include all departments of psychology. It has the general interest that is always aroused by the breadth of view of its brilliant author.

J. E. Trevor

The Elements of the Differential and Integral Calculus. *By J. W. A. Young and C. E. Linebarger. 15 × 21 cm; pp. xvii + 410. New York: D. Appleton and Company, 1900. Price: $2.20.* — In 1895, under the title *Einführung in die mathematische Behandlung der Naturwissenschaften*, Nernst and Schoenflies published their well-known introduction to the calculus, for the use of students of the physical sciences and with especial reference to applications in chemistry. The book was widely used, and was followed by a revised edition (3, 166) three years later. The manifest advantages of a simple treatment of this sort, accompanied by illustrative examples taken from the physical sciences, have led Messrs. Young and Linebarger to undertake the preparation of a similar treatise in English. They have based their work upon that of Nernst and Schoenflies, but have made many minor improvements, and have used the method of limits throughout. The result is a very satisfactory brief first-book, and one that will be a great help to those who have to get up some practical knowledge of the subject by themselves.

The book begins with a long chapter on analytic geometry, in which is presented all the material that is presupposed later. An introductory chapter on limits leads up to the fundamental conceptions of the differential calculus and the differentiation of simple functions. Then come the fundamental conceptions of the integral calculus, the simpler methods of integration, applications of the integral calculus, and a chapter on definite integrals. Next appear higher derivatives, functions of several variables, series, and maxima and minima; and the book is concluded by an excellent chapter on differentiation and integration of functions found empirically, taken without change from the German text.

J. E. Trevor

A Brief History of Mathematics. *An authorized translation of Dr. Karl Fink's Geschichte der Elementar-Mathematik, by W. W. Beman and D. E. Smith. 13 × 19 cm; pp. xii + 333. Chicago: The Open Court Publishing Co., 1900. Price: cloth, $1.50.* — A new volume in the Open Court Company's interesting series of popular books on mathematics is an English translation of Fink's *History of Elementary Mathematics.* Fink adopts a topical arrangement, and considers successively number-systems, arithmetic, algebra, geometry, and trigonometry. The book is an attractive one, and should appeal to anyone who is interested in a general way in the history of mathematics.

J. E. Trevor

Elements of the Differential Calculus. *By James McMahon and Virgil Snyder. 14 × 20 cm; pp. xiv + 337. New York: American Book Company.*— This is a revised edition of a recent college textbook on differential calculus, designed especially to meet the needs of engineering students. Although it is very modern, in its rigorous style of treatment, it has nevertheless been kept simple and clear. The illustrative exercises are happily enlivened by an admixture of physical problems. As a first-book, it is pretty comprehensive, including a chapter on the expansion of functions, and several on functions of more than one variable; while a third of the volume is devoted to applications to plane geometry, an interesting feature of which is a chapter on curve tracing. With such a generous amount of matter, it seems a pity, especially from the point of view of the physical chemist, that the treatment could not have been rounded out by an account of the more prominent properties of algebraic surfaces. Still, the book is an excellent one; and it conveys, clearly and in small compass, a great deal of important information.

J. E. Trevor

Scientific Papers. *Vol. I. By John William Strutt, Baron Rayleigh. 18 × 27 cm; pp. xiv + 562. (The Cambridge University Press). New*

York: The Macmillan Company, 1899. Price: cloth, $5.00. — The present volume is an important addition to the list of Collected Papers of prominent men of science. That Lord Rayleigh's many years of activity have been brilliant, and fruitful of results, is made strikingly evident by this collection of the seventy-eight papers published by him during the twelve years from 1869 to 1881. Only enthusiastic devotion to science, on the part of a man of unusual ability, could have produced such a showing. But little of Lord Rayleigh's earlier work, however, has had a direct bearing upon chemistry; the articles here that have a particular chemical interest are the well-known papers of 1875: On the Dissipation of Energy; and On the Work that may be Gained during the Mixing of Gases. A larger proportion of work relating to chemistry is to be expected in the forthcoming second volume. In respect of mechanical execution, the Cambridge University Press has produced here an exceedingly handsome book.

J. E. Trevor

A Textbook of Physics. *By W. Watson. 14 × 20 cm; pp. xxii + 896. New York: Longmans, Green and Co., 1899. Price: cloth, $3.50.* — This new elementary textbook of physics is a somewhat bulky volume, in which a comprehensive account of experimental physics is given in a natural order and with careful explanation of difficult points. The arrangement is much the usual one; but with the introduction, at the proper places, of considerable new material, notably in regard to changes of state and electrochemistry. The phase rule, however, is left out. Mathematical description is used most sparingly. The illustrations are sensible, being largely diagrammatic. In accordance with the introductory character of the book, citations of the literature are omitted. On the whole, the book appears to give about as good an introductory treatment of experimental physics as one can find in a one-volume work. *J. E. Trevor*

Le Phénomène de Zeeman. *Par A. Cotton. (Scientia, No. 5.) 13 × 20 cm; 100 pp. Paris: Georges Carré et C. Naud, 1899. Price: 2 francs.* — This little book gives a succinct account of what has been learned from experiment in regard to the magneto-optic 'phenomenon' of Zeeman. It begins with a brief *résumé* of the recent developments of spectrum analysis, which led to Zeeman's discovery; and then discusses successively the causes that affect the spectral rays, and the history of the discovery itself; the changes of rays of emission as observed parallel to and perpendicularly to the magnetic field; the effect of the magnetism upon the absorption of the rays; and the later development of the subject. An exposition of the theories that have been advanced is not attempted, as being of necessity premature. *J. E. Trevor*

Grundzüge der kinetischen Naturlehre. *By Baron N. Dellingshausen. 15 × 23 cm; pp. viii + 520. Heidelberg: Carl Winter, 1898. Price: 10 marks.* — This book is an attempt to account for all physical processes in terms of the movements of a material substratum devoid of properties. It may thus be regarded as an outline treatise on physics, written from the standpoint of the crudest kind of old-fashioned materialism. In this age of the world, the interest of such a book is largely archaeological — or pathological.

J. E. Trevor

REVIEWS

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

General

Thermodynamics. *K. Wesendonck. Wied. Ann.* 69, *809* (*1899*). — A general discussion of the progress that has been made by investigators to fulfil the hope expressed by Clausius in 1867, that the second law of thermodynamics might be expressed in as simple and natural a way as the law of the conservation of energy. *H. T. B.*

Asymmetric nitrogen. *J. A. Le Bel. Ber. chem. Ges. Berlin*, 33, *1003* (*1900*). — The use of the culture method in the isolation of optically active compounds cannot be wholly dispensed with, as in many cases it is impossible to form crystalline compounds with active substances. The concentration at which the organism grows most abundantly must be first ascertained by experiment. At times a mycelium may form which does not attack one of the isomers. Care must therefore be taken not to assume the absence of an asymmetric compound. Here traces of empyreumatic or aldehyde compounds are often sufficient to completely inhibit growth of the organism. The use of antiseptics, especially mercuric chloride, must be avoided. A temperature of 15°–20° is the most favorable for fermentation, as at higher temperatures parasitic bacteria flourish which prey on the mould. *C. G. L. W.*

The distillation of amalgams and the purification of mercury. *G. A. Hulett. Zeit. phys. Chem.* 33, *611* (*1900*). — Mercury can be distilled without difficulty in a partial vacuum if air be let in as is done when distilling organic substances. Zinc and cadmium do not pass over with the mercury, but zinc oxid is carried over, probably mechanically. To test the purity of a sample of mercury, the author measures the electromotive force of a cell Zn | zinc salt, mercuric oxid | mercury. [It would be better to make this a zero method by using as the electrodes pure mercury and the mercury to be tested.]

W. D. B.

Revision of the atomic weight of iron. *T. W. Richards and G. P. Baxter. Zeit. anorg. Chem.* 23, *245* (*1900*). — From the reduction of ferric oxid, the authors find 58.88 as a preliminary value for the atomic weight of iron.

W. D. B.

Peruranic, permolybdanic, pertungstic, and the other corresponding acids. *L. Pissarjewsky. Zeit. anorg. Chem.* **24**, *108* (*1900*). — Thermochemical measurements. *W. D. B.*

One-Component Systems

Density determinations of saturated vapors and liquids. *R. F. von Hirsch. Wied. Ann.* **69**, *456* (*1899*). — By the method devised by Young, the relation of the volumes of a liquid and its vapor, in a closed tube at different temperatures up to the critical temperature, is studied for several organic substances. The results have led the author to speculate a little on the true meaning of the critical temperature. The two curves of density and temperature for the liquid and vapor, or pressure and specific volume, have a common maximum or "critical" point, according to the ideas of Van der Waals, which the author considers does not really exist. On the contrary, he introduces the idea of a "critical" density as a third variable to the "critical" temperature and "critical" pressure to explain the difference still apparently existing in the density of the saturation curve for liquid and gas at the "critical" temperature, or the temperature at which the meniscus disappears. The author further introduces the question whether a "reduced" or "corrected" equation of condition can really be said to exist. *H. T. B.*

On the specific heat of metals at low temperatures. *U. Behn. Drude's Ann.* **1**, *257* (*1900*). — A continuation of the work by the same method used by the author previously (**3**, 176) The metals Sb, Sn, Cd, Ag, Zn and Mg are studied together with graphite and several zinc and lead alloys. In all cases a decrease in specific heat with decreasing temperature was noted for observations at + 18°, 0°, − 79°, and − 186°, according to a parabolic law. Various tables are prepared and an attempt made to show the dependence of the specific heat on the relation of the atomic weight and atomic volume. *H. T. B.*

On the heat of sublimation of CO_2 and the heat of vaporization of air. *U. Behn. Drude's Ann.* **1**, *270* (*1900*). — In the author's previous work the mean specific heat of several of the metals is given between + 18° and − 79°, and + 18° and − 186°. A method is here adopted for determining the heat of vaporization of air and the sublimation heat of CO_2 by introducing into a suitably protected vessel containing either of these substances a piece of metal of known weight and temperature, and thereby imparting a definite and known quantity of heat. This heat is used in either boiling the liquid air or in subliming the solid CO_2. The amount of gas given off is collected and measured in a gasometer. A few sources of error are discussed and the methods adopted of avoiding them described. The result for air is found to be 50.8 calories, and for CO_2 142.4 calories. By the aid of the results the density of air and CO_2 at − 183° and − 79° is estimated. *H. T. B.*

On adiabatic changes of condition of a system composed of a crystal and its melt. *G. Tammann. Drude's Ann.* **1**, *275* (*1900*). — The isentropic change of a crystal in equilibrium with its melt is shown to lead to the conclusion that the equilibrium is, in many cases, not greatly disturbed by the process, and that in view of this the principal thermal properties can be connected by simple equations. *H. T. B.*

Measurement of low temperatures. *A. Ladenburg and C. Krügel. Ber. chem. Ges. Berlin*, 32, *1818* (*1899*). — The apparatus of Holborn and Wien has been compared with the hydrogen thermometer at three points and the intervening points calculated by means of a cubic equation. This calculation was controlled by observing a fourth point.

A large number of boiling-points and melting-points were observed.

C. G. L. W.

Measurement of low temperature. *A. Ladenburg and C. Krügel. Ber. chem. Ges. Berlin*, 33, *637* (*1900*). — See foregoing abstract. The boiling- and melting-points have been re-examined. Differences of 1°-2° were found from those previously obtained. *C. G. L. W.*

The hardness of simple substances. *J. R. Rydberg. Zeit. phys. Chem.* 33, *353* (*1900*). — It is shown that the hardness of the elements is a periodic function of the atomic weight. *W. D. B.*

On a method for determining the inversion point of monotropic dimorphous substances. *R. Schenck. Zeit. phys. Chem.* 33, *445* (*1900*). — The author determines the relative pitch of the two curves for solid and vapor from the freezing-point constants, and then determines, by extrapolation, the temperature at which these two curves would intersect. In this way, a value of 105.9° is obtained for the inversion temperature with the two forms of *m*-nitro-*p*-acettoluid in equilibrium. In the case of monochloracetic acid the two curves appeared to be parallel. *W. D. B.*

The physical properties of cesium. *M. Eckhardt and E. Graefe. Zeit. anorg. Chem.* 23, *378* (*1900*). — The specific weight of liquid cesium at 27° is 1.836, of solid cesium at 26° is 1.886. The melting-point is 26.37°; the atomic heat is 6.406; and the heat of fusion is 3.73 cal. per gram. *W. D. B.*

Two-Component Systems

The solubility of carbonic acid in alcohol between —67° and + 45° C; invasion and evasion coefficients at 0°. *C. Bohr. Drude's Ann.* 1, *244* (*1900*). — Two methods are used to determine the solubility of CO_2 in alcohol; one by saturating with the gas at different temperatures and finding the amount of dissolved CO_2 in a given quantity of alcohol, and the other more particularly for use at low temperatures, by determining the amount of gas given off on lowering the temperature of saturated alcohol from 0°. The measurements of the invasion and evasion coefficients are made in a similar way to that described in the author's previous works (2, 400; 4, 145). On comparing the results with water it is shown that the relatively large absorption coefficient of the alcohol for CO_2, notwithstanding its evasion coefficient being nearly seven percent greater than for water, gives an invasion coefficient eighteen times greater than for water. Alcohol becomes much more quickly saturated with CO_2. so much so that if at 0° the ratio of the surface to the volume be 1/5, then the same degree of saturation is reached in alcohol at the end of ten minutes, that is reached in water at the end of sixty-eight minutes. *H. T. B.*

On compounds in alloys. *N. S. Kurnakow. Zeit. anorg. Chem.* 23, *439* (*1900*). — The freezing-point curve of sodium and mercury shows seven different solid phases capable of existing in equilibrium with solution and vapor above 0°. There is one temperature maximum corresponding to the composition $NaHg_2$. Between Na and $NaHg_2$ there are four solid phases, three of which are probably solid solutions, while one appears to be NaHg. The solid phase appearing beyond the maximum temperature may be $NaHg_4$ or may not.

The curve for potassium and mercury could not be determined close to the potassium end, but there is a maximum freezing-point at the composition KHg_2. On the potassium side, the curve for this compound is terminated by the curve for a solid solution; on the mercury side, there is evidence pointing to the existence of KHg_3, after which come two solid phases, one of which may be KHg_{10}.

With cadmium and sodium there is one maximum freezing-point at $NaCd_2$, and another at about $NaCd_4$. With sodium and lead there are two maxima, one of which is not far from Na_2Pb, while the other is distinctly not Na_2Pb. With sodium and bismuth there is a maximum at Na_3Bi. *W. D. B.*

A relationship between the specific heat of solutions of cobalt chlorid and their color. *M. Wresky. Jour. Russ. Soc.* 31, *164* (*1899*). — Solutions of cobalt chlorid in aqueous alcohol were found to have a lighter color and smaller specific heat, the less the proportion of dissolved salt. Similar change of color and specific heat were brought about by lowering the temperature. *C. E. L.*

On the specific heat of aqueous solutions of sulfuric acid. *E. Biron. Jour. Russ. Soc.* 31, *171* (*1899*). — The concentrations varied from the monohydrate to one mol of the monohydrate mixed with 1600 mols. of water. Full tables are given for the results obtained. The curve accompanying the paper shows that with increasing strength of the acid solution, its specific heat at first diminishes until at about 27 percent H_2SO_4 it commences to increase, attaining a maximum in the neighborhood of 48 percent; and then after falling off to the lowest value at about 86 percent, it attains a second (lower) maximum at about 95 percent. *C. E. L.*

The hydrates of sulfuric acid. *E. Biron. Jour. Russ. Soc.* 31, *517* (*1899*).— Crystals were obtained whose composition corresponded to the formulae H_2SO_4 (10.35°); $H_2SO_4.H_2O$ (8.53°); $H_2SO_4.2H_2O$ (− 38.9°); $H_2SO_4.4H_2O$ (−29.0°); the bracketed numbers are the melting-points of the crystals. *C. E. L.*

On the freezing-point of aqueous solutions of non-electrolytes. *E. H. Loomis. Phys. Rev.* 9, *257*; *Zeit. phys. Chem.* 32, *578* (*1900*). —In the earlier measurements the thermometer was kept completely packed in ice when not in use. Since the room temperature was about + 5°, it is clear that the stem of the thermometer had been supercooled and that the first measurements each day, those on the freezing-point of pure water, would necessarily be slightly wrong.

The result of the most recent and the most accurate experiments is that the constant for aqueous solutions of propyl alcohol, butyl alcohol, amyl alcohol, glycerol, acetone, grape sugar, cane sugar, mannit, and anilin is 1.86; while it is 1.82 for methyl alcohol, 1.84 for ethyl alcohol, and 1.50 for ether. The exceptions may be due to the volatility of the three substances. *W. D. B.*

Solidification and inversion phenomena with optical antipodes. *J. H. Adriani. Zeit. phys. Chem.* 33, *453* (*1900*). — Racemic compounds occur with dimethyl tartrate, dimethyl diacetyl tartrate, mandelic acid, and benzoyl tetrahydroquinaldin. All mixtures of the two camphor oximes freeze at the same temperature, 118.8°, the solid phase being a solid solution of the two antipodes, as is shown by the fact that the racemic compound is instable above 103°. With the two carvoximes, a continuous freezing-point curve was obtained, passing through a maximum at 91.4°. It seems probable that, in this case, the solid phase consists of a solid solution of the racemic compound with one or the other of the components; but there is no way of proving it at present. *W. D. B.*

The effect of pressure on the critical solution point. *N. J. van der Lee. Zeit. phys. Chem.* 33, *622* (*1900*). — Increase of pressure causes phenol and water to become less miscible. *W. D. B.*

Poly-Component Systems

Racemic compounds. *I. Schlossburg. Ber. chem. Ges. Berlin*, 33, *1082* (*1900*). — The investigation of double salts of racemic, pyrotartaric, tropaic and mandelic acids, according to the method of Roozeboom and Ladenburg, shows that in these compounds a racemic modification is present. *C. G. L. W.*

Active oxygen. *C. Engler. Ber. chem. Ges. Betlin*, 33, *1090* (*1900*). — The absorption of oxygen by substances such as triethyl phosphin or benzaldehyde takes place in such a way that half of the oxygen only will subsequently be given up to oxidize substances such as indigo or arsenious acid, while the other half remains with the "autoxydator". Although the existence of a compound belonging to the peroxid class has been shown by Engler and Weissberg (Ber. chem. Ges. Berlin, 31, 3046 (1898)), a similar behavior to the first mentioned substance has not as yet been proved. Titration of the active oxygen with stannous chlorid has not been found successful. The use of indigo sulfuric acid shows that the amount of oxygen given up by the turpentine is equal to very nearly fifty percent of the total absorbed.

Direct estimation of the amount of oxygen absorbed by pinene shows that one molecule of the terpene absorbs between four and five molecules of oxygen.

Experiments with unsaturated hydrocarbons, viz., amylene, trimethylene, ethylene, and hexylene, proved the absorption of a definite amount of oxygen by the compounds. In the case of amylene a certain part of the oxygen is used up to form a peroxid as the titration with stannous chlorid showed. A large number of unsaturated compounds, especially those of the allyl series, absorb oxygen, forming peroxids. In many cases the compounds act as direct oxygen carriers, bleaching indigo sulfuric acid in the presence of air. *C. G. L. W.*

Active oxygen. *C. Engler. Ber. chem. Ges. Berlin*, 33, *1097* (*1900*). — Van 't Hoff has shown that atmospheric oxygen in certain oxidation processes is divided in its action. One-half goes to the directly oxidizable compound (autoxydator). The other half is combined with a compound which is not directly oxidizable (acceptor). According to van 't Hoff, the action is due to a certain amount of the gas being ionized into positive and negative oxygen of which the one is used up by the autoxydator while the other unites with the acceptor. No electric phenomena have so far been brought forward to support this view. The view of Engler and Wild may be used to explain the facts in which the formation of peroxid is assumed. Hence the reaction processes in the following phases:

$$A + O_2 = AO_2;\ AO_2 + B = AO + BO,$$

where A represents e. g. triethylphosphin and B indigo sulfuric acid. A may also react instead of B giving

$$A + O_2 = AO_2;\ AO_2 + A = AO + AO.$$

This is supported by the experiments of M. Franke on oxidation by molecular oxygen in the presence of water, where the formation of hydrogen peroxid is assumed to take place. The combustion of rubidium in air, by which only rubidium peroxid is formed is also in favor of this view. A number of interesting examples of oxidation in terpene, waxes, paraffins, oils, and resins is cited. In those cases where quantitative methods have been used, it has been found that the oxygen taken up was double that required for a simple oxidation. In these cases, however, where an acceptor is present, the oxygen will be equally divided between it and the autoxydator. This is to be seen in the formation of benzoylsuperoxid. The reaction is complicated by the formation of a superoxid hydrate. From consideration of autoxidation, the author comes to the following conclusions:

I. Oxygen combines directly with unsaturated compounds forming peroxid.

II. Oxygen may combine with a labile hydrogen atom of the autoxydator forming hydrogen peroxid. The radical takes up another atom of oxygen forming a peroxid.

III. Oxygen may combine with a labile hydrogen atom of the autoxydator forming hydrogen peroxid. The radicle is not oxidizable and remains as such or double. The possibility is mentioned of the oxidation taking place with molecular oxygen and not with the element in the atomic state. The influence of light in oxidation may arise from increase in the active state of the molecule or may arise from a breaking of one of the bonds forming oxygen in the state .O.O. or O ⁝ O, or perhaps that the oxygen dissolved in the autoxydator is rendered active by light. *C. G. L. W.*

Active oxygen. *C. Engler. Ber. chem. Ges. Berlin*, 33, *1109* (*1900*). — This paper is concerned with a demonstration of the formation of hydrogen peroxid and other peroxids as products of direct oxidation. Purified hydrogen is burned in air. The flame impinges against a piece of ice. Hydrogen peroxid may be recognized in the ice water by the usual tests. That the peroxid is not formed by direct oxidation of the water through the heat of the flame is proved by using a platinum wire raised to a white heat which is placed in ice water. No hydrogen peroxid is formed even after contact of the wire with the water for some hours.

The formation of peroxids may be detected by a suitable arrangement of burning carbon monoxid, illuminating gas, alcohol, ether, and carbon bisulfid. Sodium and magnesium also form peroxids which may readily be detected.

C. G. L. W.

Double metallic rhodanids. *A. Rosenheim and R. Cohen. Ber. chem. Ges. Berlin*, 33, *1111* (*1900*). — Salts of the type $RHg(SCN)_3$ have been studied. They are in contradistinction to those of the type $R_2Hg(SCN)_4$ difficultly soluble in water. Conductivity-increase went to show that in both cases the anion consists of a rhodan mercury ion. Double salts of cobalt, nickel, and aluminium and chromium rhodanids with the alkalies and alkaline earths were prepared. In dilute alcoholic solution the cobalt is found as a part of the anion. In the corresponding nickel salt, the nickel is found in the cation. *C. G. L. W.*

Deduction of the reaction isotherm and isochore for dissociating mixtures. *K. Ikeda. Zeit. phys. Chem.* 33, *287* (*1900*). — The chief novelty of the treatment consists in the assumption of two ideal non-miscible solvents, in one of which there is no dissociation, in the other of which there is complete dissociation. *W. D. B.*

Change of solubility by salts. *V. Rothmund. Zeit. phys. Chem.* 33, *401* (*1900*). — The author finds that the solubility of phenyl sulfocarbamid in water is changed by the addition of salts, and that the percentage change does not vary perceptibly with the temperature between 0° and 40°. The author appears to think that he is opening up a new field. Without quite agreeing with this view, the reviewer is glad to learn that, in the author's opinion, the subject is of the greatest importance in working out a theory of solutions. *W. D. B.*

Osmotic Pressure and Diffusion

Simple deduction of van 't Hoff's law of osmotic pressure. *K. Ikeda. Zeit. phys. Chem.* 33, *280* (*1900*). — This is merely another way of deducing the van't Hoff formula. The original van 't Hoff deduction was straightforward, and enabled everyone to see what assumptions were made. The so-called improvements strive to make the formulas appear absolute, by masking the assumption. *W. D. B.*

Velocities

On the constants of the speed of formation of simple ethers. *W. Zagrebin. Jour. Russ. Soc.* 31, *19* (*1899*). — The reaction studied was that of benzene sulfonic ethyl ether on methyl, ethyl, propyl, isobutyl, isoamyl, octyl, allyl, benzyl, isopropyl, and caproyl alcohols, and on tri-methyl and dimethethyl carbinols, the products being the corresponding ethers and benzene-sulfonic acid. The acid was titrated against *n*/20 baryta water with phenol-phthalein as indicator. Equimolecular quantities of alcohol and benzene sulfonic ethyl ether when heated to 100° separated into layers before the completion of the reaction, and the addition of a dilutent such as benzene, acetone, etc., did not help matters, as benzene-sulfonic acid is too insoluble in them. When, however, fifteen times as much alcohol as sulfonic ether were heated to 100°, the reaction was practically completed in a few hours.

The comparison of the constants for the primary alcohols exhibits a fairly close parallelism with those obtained by Menschutkin for the compound ethers and amins, and the rule that the constant for tertiary alcohols are notably smaller than those for the primary and secondary alcohols are confirmed, although side-reactions seemed to interfere in the case of the tertiary alcohols. *C. E. L.*

Some remarks on the subject of the investigation of the speed of formation of simple ethers. *N. Menschutkin. Jour. Russ. Soc.* 31, *28* (*1899*). — Notes on Zagrebin's work (preceding review) together with a program for future investigations along similar lines. *C. E. L.*

Chemical kinetics and free energy of the reaction: $2HI + 2Ag \rightleftarrows 2AgI + H_2$. *H. Danneel. Zeit. Elektrochem.*, 6, *293* (*1899*); *Zeit. phys. Chem.* 33, *415* (*1900*). — Silver, silver iodid, and hydrogen are in equilibrium with aqueous hydriodic acid when the concentration of the latter is *n*/0.042. From reaction velocity experiments, the author concludes that the hydrogen enters into the reaction as H_1 and not as H_2.

Attempts to confirm the equilibrium phenomena by electrometric measurements led to the unexpected result that good values are obtained when hydrogen is not made to bubble through the solution, while they are 0.02 V too high when this is done. *W. D. B.*

Electromotive Forces

On the stationary temperature condition in an electrically heated conductor. *F. Kohlrausch. Drude's Ann.* 1, *132* (*1900*). — A new method is proposed for the purpose of studying the flow of heat in a long cylindrical metal rod heated by the passage of an electric current, and insulated thermally except at the two ends, which are maintained at a constant temperature. The position of the isothermal and isopotential surfaces are then transverse to the length of the rod. Only the theory of the method is treated of in the present paper, which should be taken in connection with the measurements of Jaeger and Diesselhorst, who have applied the method to the case of several metals and alloys. The author shows that the steady temperature condition does not depend on thermal or electrical conductivity alone, but on the ratio of the two. The pure metals form a group giving the smallest value of this ratio and at the same time the highest temperature. *H. T. B.*

On the problem of an electrically heated conductor. *H. Diesselhorst. Drude's Ann.* 1, *312* (*1990*). — This is an extension of the paper by Kohlrausch in which he proposed and treated theoretically a new method for determining the ratio of the thermal and electrical conductivities in metals by the steady temperature condition set up in a metal bar heated by an electric current. The author treats the case of a change of conductivity with temperature, and also the Thomson effect, which has to be considered in using the method. A better form of this method was proposed by Callendar, and worked out by R. O. King in 1898 and R. G. Duncan in 1899. *H. T. B.*

Potential differences with manganese peroxid electrodes. *O. F. Tower. Zeit. phys. Chem.* 32, *566* (*1900*). — Further measurements which do not add materially to our knowledge of the subject. *W. D. B.*

On decomposition points in aqueous solutions. *A. Gockel. Zeit. phys. Chem.* 32, *607* (*1900*). — Measurements are published to show that there is no definite decomposition voltage, and that the point usually observed is that at which there is visible precipitation, which may vary considerably with the conditions of the experiment. There is no doubt but that the absorption of gases and the roughness of surface is a factor. With the precipitation of metals, there is the further possibility that, at given voltages, the metal may not have the properties of matter in mass, in which case the time element would vary with the size of the electrode. This side of the question is not brought out by the author, and, in other respects, one cannot congratulate him on the way he handles his experimental data. *W. D. B.*

Reversible electrodes of the second class, with mixed depolarizers. *A. Thiel. Zeit. anorg. Chem.* 24, *1* (*1900*). — The author has determined the electromotive force of silver covered with mixed silver halids against the normal electrode. Silver chlorid and silver bromid form a continuous series of mix crystals and the potential varies continuously. Silver bromid and silver iodid form two series of mix crystals; but the potential is practically that of silver bromid most of the way and then changes rapidly to that of silver iodid. This is interesting, though not what one would have expected. *W. D. B.*

Electrolysis and Electrolytic Dissociation

Conductivity of some sodium-substituted nitroparaffins. *O. Sulc. Zeit. phys. Chem.* 32, *625* (*1900*). — The author has determined the conductivity of solutions of sodium nitromethane, sodium nitroethane, sodium nitropropane, sodium nitro-isopropane, and sodium nitro-isobutane. At a dilution of one thousand liters, the molecular conductivities lie between 80 and 109. *W. D. B.*

On the hydrolysis of some chlorin compounds of platinum, gold and tin, caused by time or sunlight. *F. Kohlrausch. Zeit. phys. Chem.* 33, *257* (*1900*). — An aqueous solution of H_2PtCl_4O undergoes almost no change in the dark; in direct sunlight there is marked hydrolysis, as shown by the increase in conductivity. The acid H_2PtCl_6 is hydrolyzed only in very dilute solutions. The acid H_2AuCl_3O is not affected by light; the platinum electrodes cause precipitation of gold. Hydrolysis takes place in solutions of $HAuCl_4$. An aqueous solution of $SnCl_4$ undergoes decomposition on standing, the change in the conductivity being proportional to the change in the logarithm of the time.

W. D. B.

On electrolysis through semipermeable membranes. *B. Moritz. Zeit. phys. Chem.* 33, *513* (*1900*). — The author has investigated the behavior of membranes formed in parchment paper. With the copper ferrocyanid membrane there is a precipitation of copper ferrocyanid so long as the polarization does not exceed 0.22 V. With ever higher potential differences there is first the formation of ferrocyanid as ion and then the precipitation of metallic copper. It is not certain whether this last phenomenon is or is not to be attributed to electrostenolysis. *W. D. B.*

On the dissociation and dissociation equilibrium of strong electrolytes. *H. Jahn. Zeit. phys. Chem.* 33, *545* (*1900*). — The author has determined the transference numbers of sodium, potassium, and hydrogen chlorids in dilute solutions. He then measured the electromotive force of concentration cells with silver and silver chlorid as electrodes. Assuming complete dissociation in *n*/600 solution, and the accuracy of Nernst's formula for concentration cells, the author calculates the dissociation in the other solutions. The values thus obtained are lower than those from the conductivity, and they follow the dilution law. The conclusion is therefore drawn that it is impossible to determine the degree of dissociation from the conductivity measurements, owing to the change of migration velocities with the concentration. *W. D. B.*

On the dependence of electric conductivity on pressure. *G. Tammann. Wied. Ann.* **69**, *767* (*1899*). — The author extends the previous work on the effect of pressure on the conducting power of dilute solutions, from 500 to 3600 atmospheres, in the case of sodium chlorid solutions and solutions of acetic acid. *H. T. B.*

The analytical separation and detection of acids. *R. Abegg and W. Herz. Zeit. anorg. Chem.* 23, *236* (*1900*). — An attempt has been made to place in analytical groups the acids met most frequently in laboratory experience. Although it is evident that sufficient care has not been devoted to the study of interfering reactions, the effort to put this analytical work on a systematic basis is worthy of commendation. There is no doubt that many chemists will comply with the wishes of the authors that the methods be tried in laboratories other than their own. *H. R. C.*

On the application of Faraday's law to the electrolysis of fused salts. *A. Helfenstein. Zeit. anorg. Chem.* 23, *255* (*1900*). — The author shows that it is very difficult indeed to get satisfactory quantitative results from the electrolysis of fused salts. The sources of error are the solubility and diffusion of metal and halogen, also the diffusion of the vapor of the metal. When these difficulties are eliminated, Faraday's law was shown to hold. The interesting item in the paper is the surprising magnitude of the 'residual current' when no precautions are taken. *W. D. B.*

On some complex cyanids and sulfocyanates. *P. Walden. Zeit. anorg. Chem.* 23, *373* (*1900*). — The author has determined the conductivity, at different dilutions, of potassium silver cyanid, potassium mercuric cyanid, potassium zinc cyanid, potassium cadmium cyanid, potassium nickel cyanid, potassium platinic sulfocyanate, potassium cobalticyanid, potassium manganicyanid, and $Na_3Fe(CN)_5NO$. *W. D. B.*

Electrosyntheses of diketones and ketones. *H. Hofer. Ber. chem. Ges. Berlin*, 33, *650* (*1900*). — Acetoacetic acid and its salts are not suitable for electrolysis on account of the ease with which they decompose.

A solution of potassium pyruvate, electrolyzed in the author's apparatus with potassium carbonate as the cathode electrolyte, gives diacetyl and acetic acid. Levulinic acid gives 2.7 octandin $\begin{array}{l}CH_3.CO.CH_2.CH_2.\\ CH_3.CO.CH_2.CH_2\end{array}$ A fifty per-cent yield was obtained. Acetic acid is also produced in the reaction.

A mixture of potassium pyruvate and acetate gives also diacetyl and acetone. With the potassium salts of pyruvic and butyric acids, methyl propyl ketone is produced. 1.5-Hexandion is formed in the electrolysis of potassium pyruvate and levulinate. The yield is small. In all the reactions large quantities of gas were given off, consisting chiefly of carbon dioxid.

C. G. L. W.

ON THE SOLUBILITY OF MANGANOUS SULPHATE

BY F. G. COTTRELL

Something over a year ago, during the discussion of some other work, Dr. Bancroft called my attention to a very interesting case of equilibrium in systems of manganous sulphate and water, studied by Linebarger,[1] among which, according to his determinations, we have several possible combinations consisting of a stable hydrate, an unstable hydrate, solution and vapor, where the stable form is the more soluble. Thus, for example, according to Linebarger, at 15° the stable form is the pentahydrate and its solubility is 72.33 parts anhydrous salt per 100 parts of water; while that of the tetrahydrate (stable from 18° to 30°) is 67.12 parts per 100 of water. Thus it seems natural to assume that if some of each hydrate were introduced into a solution, containing say 70 parts salt to 100 parts of water, the stable form would dissolve and the unstable form be precipitated; unless it be possible to form two solutions of the same concentration, but differing in their properties, depending upon which hydrate they were made up from.

It was with the hope of throwing some light on this matter that the present work was undertaken. It soon became manifest that the greater part at least of the peculiarities of these systems are to be explained by inaccuracies in Linebarger's solubility determinations, and the problem then resolved itself into a redetermination of these and this it is that forms the major part of this present paper.

The solubility of this salt has received the attention of a number of workers previous to this time. Brands[2] seems to be the first whose results are worthy of attention at the present day.

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[1] Amer. Chem. Jour. 15, 225 (1893).

[2] Pogg. Ann. 20, 556 (1830).

His methods were rather crude and the data are of interest more in a qualitative than a quantitative sense. Étard[1] has also given us some values and deduced from them linear equations connecting solubility with temperature, but the experimental data presented are so meagre that it becomes practically impossible to coordinate them with later work. Mulder[2] determined the solubility from 0° to 102.5°, using the tetrahydrate as solid phase to start with, which is a very indefinite statement of the conditions as will be seen from what follows. His results are all somewhat higher than those here presented, and diverge more from these as the temperature rises. They are, however, all lower than those of Linebarger. I have been unable to procure Mulder's original papers and the abstracts which are available give nothing of the experimental details.. Since the publication of Linebarger's papers, Stortenbeker[3] has called attention to the improbable character of his curves, but seems to have made no experiments on the matter.

Linebarger's work includes the hydrates with 1, 2, 3, 4, 5, 6, and 7 molecules of water of crystallization. The only hydrates which I have been able to prepare are those with 1, 4, 5, and 7 of water, which of course need only mean that the exact conditions required for the separation of the others have not been realized; but it probably indicates that, if they are stable at any temperature, their solubility curves lie close to those of the other hydrates, and the salts have little tendency to crystallize from their supersaturated solutions.

Of these other hydrates, the one with six molecules of water was obtained by Brands[4] on drying the heptahydrate between folds of filter-paper at 8° to 10°. As the transition point from heptahydrate to pentahydrate is about 9°, it seems quite likely that Brands was dealing with a mixture of these two. Linebarger obtained the salt as hexagonal plates by cooling a

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[1] Comptes rendus, 106, 208 (1888).

[2] Scheik. Verhandel, Rotterdam, p. 137 (1864).

[3] Stortenbeker. Zeit. phys. Chem. 17, 648 (1895).

[4] Pogg. Ann. 20, 569 (1830).

solution "containing about 80 pct. of anhydrous salt"[1] into a temperature of 2° to 5° until crystals separated. Some of these were then sown in a solution kept at 0° and thus well-formed crystals prepared.

During the present investigation, a number of attempts were made to prepare this salt by cooling strong solutions to 0° and also a few degrees above and below, but it was always the heptahydrate that separated out. Expecting that the hexahydrate, if it existed, would probably be isomorphous with those of zinc or magnesium, crystals of these were introduced into the supercooled solutions, but they gradually dissolved and eventually a separation of heptahydrate set in (see det. 117).

As to the trihydrate, Linebarger seems to be the only one who has separated it in well-formed crystals. Brands' method for its preparation consisted in treating the higher hydrate with boiling absolute alcohol or oil of turpentine, also by allowing the anhydrous salt to absorb moisture from the air; and he sometimes found it mixed with tetrahydrate in the crystallization of the latter. Linebarger quotes Graham as the only previous investigator who has mentioned the spontaneous crystallization of the trihydrate from solution. Playfair[2] however obtained it as a crust on the surface of a boiling saturated solution. These crusts were removed and rapidly dried between folds of filter-paper. Linebarger himself prepared it both by the dehydration of the tetrahydrate with 98 percent of alcohol at 20° for a month, and also by crystallizing aqueous solutions at 33° to 35°. The dihydrate was obtained by Brands on melting the heptahydrate in its water of crystallization and also by heating it to about 80° with 55 percent alcohol. Linebarger found that it formed as a crust over the surface of a solution evaporated on the water-bath

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[1] By this is probably meant a solution containing 80 parts of anhydrous salt to 100 parts of water, as the most concentrated solutions given by Linebarger do not exceed 88 parts of salt to 100 parts of water, and even this value is probably much too high, on account of his method of analysis, which is to be discussed later.

[2] Quoted by Thorpe and Watts, Jour. Chem. Soc. (Lond.) 37, 113 (1880) from previously unpublished manuscript.

and also secured well-formed crystals by evaporating a solution in the thermostat at 40° to 45°. He found the same salt was likewise produced when a layer of strong solution of the salt was allowed to diffuse into concentrated sulphuric acid.

The salts used in the following work were prepared by recrystallizing the manganous sulphate from three different factories, viz.: Merck and Co., New York; Rosengarten and Sons, Philadelphia; and Mallinckrodt Chemical Works, St. Louis. Both the Merck and Mallinckrodt were found to be the tetrahydrate, while the Rosengarten preparation was the pentahydrate. The only appreciable impurities in these appeared to be traces of calcium and aluminium sulphate which were pretty effectually removed by the recrystallization. Even in the monohydrate, where these would be most apt to put in an appearance, they did not exceed 0.1 percent.

The monohydrate used in the determinations was prepared by saturating a solution at about 30° to 40° with one of the higher hydrates and, after filtration, bringing the clear liquor to a boil with constant stirring. The monohydrate thus precipitated was rapidly filtered off with the aid of the filter-pump and most of the mother-liquor removed in the same way. It was then transferred to an air-bath at 100° to 130°, where it remained for an hour or two, being ground to fine powder a little while before the heating was concluded. For the water content and treatment of the individual samples, see Table I.

TABLE I

Det. No.	Pct. of H_2O	
		Monohydrate
—	10.66	Theoretical, calculated for $MnSO_4 + H_2O$.
95	11.10	Crystallized slowly at 43° to 48°.
96	10.75	Same material as det. 95.
97	11.24	Thin crystalline plates, crystallized at 45 ±.
98	11.33	Made by drying tetrahydrate (det. 107) at 90° to 130° for 4 hours, weighing this as monohydrate, then heating to 280° to 300° and weighing as anhydrous.

TABLE I—(*Continued*)

Det. No.	Pct. of H_2O	
99	10.77	Made by drying det. 16 at 100° to 120° for 3 hours, and weighing as monohydrate before last heating of 2 hours at 280°.
100	10.88	Same method as 99 applied to det. 17.
101	10.81	Materials prepared by bringing clear sol. of Rosengarten and Son's pentahydrate saturated at about 40° or 50° to boil, filtering with suction, and drying 3 or 4 hours at 100° to 120°.
102	10.91	Prepared as in det. 101 except that tetrahydrate from Mallinckrodt Chem. Works was used as starting-point, and drying was effected at 100° to 150° for about an hour.
		Tetrahydrate
—	32.29	Theoretical, calculated for $MnSO_4 + 4H_2O$.
103	32.84	Merck's tetrahydrate freshly ground from large lumps. Dehydration effected at 200°.
104	31.81	Same material as det. 103 after standing in sat. sol. for a few days at 30° to 33°.
105	32.00	Crystallized at 30° to 40°.
106	32.57	Crystallized at 30° to 40°.
107	32.19	Selected crystals formed at 30° to 40°.
		Pentahydrate
—	37.36	Theoretical, calculated for $MnSO_4 + 5H_2O$.
108	37.21	Crystallized rapidly in vacuo over H_2SO_4.
109	36.35	Rosengarten and Son's, taken directly from original package.
110	37.05	Crystallized at 13° ± by slow evaporation over H_2SO_4. Large perfect crystals.
111	39.6	Started for preparation of heptahydrate. Strong solution surrounded with ice, the whole placed in sawdust, and left over night. In the morning, temperature 10°. Crystals dried quickly with filter-paper.
		Heptahydrate
—	45.70	Theoretical, calculated for $MnSO_4 + 7H_2O$.
112	46.34	Crystals slightly damp. Crystallized at 0°.
113	44.24	Crystallized by cooling strong sol. to 0°, filtered off and aspirated for 3 hours, and dried in desiccator 1 hour.

TABLE I—(*Continued*)

Det. No.	Pct. of H_2O	
114	44.17	Same material as det. 113, but not placed in desiccator. Made two days later when crystals had partly liquefied.
115	46.28	Precipitated from strong solution by cooling to − 10°. Filtered and aspirated 2 hours in funnel packed in ice. Still slightly damp.
116	47.7	Another mixture treated as in det. 115. Aspirated a shorter time. Crystals still quite damp when taken for analysis.
117	49.06	Crystals prepared by cooling saturated solution of pentahydrate with ice and introducing crystal of $ZnSO_4 + 6H_2O$ (see p. 639). Crystals dried rapidly between filter-paper, but still damp.

In order to make sure that the final heating had no effect upon the solubility of the hydrate, parallel determinations were made upon some of the moist material removed from the funnel after aspirating off the mother-liquor, and also that which had been dried in the oven. Determinations Nos. 73, 77, and 78 are on the damp hydrate, while Nos. 72, 74, 75, and 76 are on the dried material and were made in the same thermostat at the same time. These two sets show as complete agreement as was to be expected.

The tetrahydrate was prepared by dissolving the commercial salt in water until a saturated solution at about 30° was formed, and after filtration placing them in a desiccator over sulphuric acid; the desiccator then being placed in a thermostat maintained at 30° to 40°. In the course of a few days, a good crop of perfectly clear and regular crystals was invariably obtained.

The pentahydrate was prepared by allowing a solution of the commercial salt to evaporate in a desiccator at the ordinary room temperature.

The heptahydrate was prepared by cooling a solution of the commercial salt, saturated at 30° to 40°, with ice and salt until the whole was several degrees below zero. If crystallization had not already set in, it was brought about by vigorous shaking, which was continued until precipitation was complete, thus leaving the salt in a finely divided form suitable for the solubility determinations. This was then rapidly filtered off in a Gooch crucible surrounded by ice, or ice and salt, and air aspirated through until the crystals were fairly dry.

The salt whose solubility was to be determined was placed in a bottle of from 8 to 20 cc capacity, depending upon the work in hand. The liquid to be saturated was then added and the bottle clamped by copper springs to the face of a wooden wheel, wholly immersed in the water of a thermostat and rotated by a small water-wheel, or, in the later work, an electric motor. In the determinations up to 33°, a bath of about 3 liters capacity was used, but from there on one of more than double this capacity was substituted. Both were covered with asbestos and provided with a modification of the Ostwald gas regulator, capable of maintaining the temperature constant within 0.2° night and day. The main supply of gas was independent of the regulator which controlled just sufficient of it to effect the necessary regulation. It required only about 0.02° change in the temperature to turn the gas completely on or off. The temperatures were read on a thermometer which had been compared with a Reichsanstalt Standard (No. 5640–1894).

When a sample of the solution was wanted for analysis, the bottles were slipped out from under the strings, the neck brought above water, carefully dried, and the stopper removed. For drawing the sample, two forms of filtering pipette were used, and in all cases they were brought to the same temperature as the solution being introduced into it. For the lower temperatures, the pipette consisted of a straight piece of glass tube 2 or 3 mm bore and about 15 cm in length. Over one end of this was placed first a bit of well-washed muslin, and over this a piece of filter-paper. The edges of these were then pressed down about the tube and wound tightly with a narrow strip of thin sheet rubber which was continued spirally up the tube to a small wire hook where the end was made fast. When enough of the liquid had been drawn up through the filter, the upper end was closed by the thumb, the filter removed, the lower end of the tube wiped clean, and the contents quickly transferred to the weighing bottles, which were small Erlenmeyer flasks with glass stoppers. For the higher temperatures, it was feared that the above pipette would necessitate too great a loss by evaporation, and it was therefore discarded in favor of the following. A capillary tube was bent into a siphon with arms of about 7 cm and 30 cm respectively. To the short arm was sealed a centimeter of larger tube, and over the end of this was fastened the muslin and filter-paper as in the other pipette, except that for temperatures above 75° platinum wire took the place of the rubber strip. The short end of the siphon was passed through a rubber stopper which fitted the bottle containing the liquid. A second hole in the stopper carried a tube through which air could be forced into the bottle, thus driving the liquid out through the filter and siphon, the longer end of which was surrounded by a small water jacket to reduce the danger of evaporation when the solution emerged.

After weighing, the Erlenmeyer flasks were placed in the air-bath at about 100° until the liquid was completely evaporated, when they were transferred to a second bath at a temperature of 270° to 280°, where they remained for an hour, and in many of the earlier determinations much longer.

Right here is where Linebarger's greatest inaccuracy seems to lie. He effected his drying at 160° to 170°, a temperature not sufficient to dehydrate the salt in any reasonable amount of time, as shown in the following determinations.

Three of the regular determinations, after drying at 100°, were heated to 170° to 180° for three and one-half hours, weighed, heated again for three hours at 270° to 280°, and again weighed, with the following results:

TABLE II

Weight of residue		Loss in weight	
After 1st heating Grams	After 2nd heating Grams	Grams	Percent on 1st weight
1.0987	0.9955	0.1032	9.4
0.6492	0.5790	0.0702	10.8
0.4425	0.3969	0.0456	10.3

From this, it is evident that at 170°, the tendency is to leave the monohydrate.

Linebarger assigns no reason for adopting the particular temperature that he did; nor does he speak of any work being done to test the accuracy of the method. This is the more surprising, as it is a commonplace statement in many text-books that the last molecule of water is not lost below 200°.

This explains why Linebarger's curves all lie above those here presented, but it does not furnish any clue as to why the determinations for the individual hydrates should lead to such smooth and regular curves, bearing such peculiar relations to one another. For this I have no explanation to offer. The temperature adopted in the present determinations (270° to 280°) is the same as used by Watts and Thorpe in their paper already referred to, and the accuracy of the method was tested in the following way.

A few cubic centimeters of a strong solution of manganous sulphate were placed in a long-necked flask of about 30 cc capacity and boiled down carefully to a solid with constant shaking, thus spreading it in a thin layer over the sides of the flask. This was then closed by a cork through which passed two small glass tubes, the first reaching nearly to the bottom, communicated directly with the outside air; while the second, reaching only to the junction of the neck with the body of the flask, was connected at its other end with a potash bulb filled with a solution of barium chloride plus a little free nitric acid. The potash bulb was in its turn connected to a filter pump. The flask and contents together with the six weighing bottles containing dets. Nos. 69 to 74 inclusive, were placed in the air-bath, which was then brought to 240° to 245° and maintained between these limits for one and one-half hours, while a slow current of air was drawn through the flask. In order to settle any question as to the possibility of this air current producing a cooling great enough to invalidate the experiment, it was interrupted for intervals of about five minutes several times during the work, but no change could be detected. Considerable water was at first deposited in the tubes, but as the heating continued, this was soon carried over by the air current into the potash bulb, the solution in which remained perfectly clear. The weighing bottles were stoppered, cooled, and weighed, then returned to the bath, and the whole carried up and held at 270° to 280° for one hour, when the weighing was repeated. Finally, the whole was heated for about three-quarters of an hour by alternately running the temperature up to 350° and down to 300°, in all about three such cycles being made. No turbidity whatever was produced in the barium solution, even on standing several days. To ascertain the sensitiveness of this test a few milligrams of sulphur were burned close to the mouth of the potash bulb and the air rapidly aspirated through. On standing, a very noticeable precipitate was produced, although the quantity of sulphur entering the bulb could not have been more than a coulple of milligrams. The weighings of the six Erlenmeyer flasks heated at the same time are given in the following table, only two being subjected to the final heating. The fact that the figures for the second heating are uniformly a little greater than for the first is probably due to the flasks having stood longer in the desiccator before the second weighing was made, i. e., it is an effect due to the condition of the glass surface of the weighing bottles:

TABLE III

		Weight of same plus $MnSO_4$		
Det. No.	Weight of flask and stopper	After 1st heating	After 2nd heating	After 3rd heating
69	11.3097	11.8706	11.8710	——
70	9.7200	10.5058	10.5060	10.5059
71	13.6030	14.1820	14.1822	14.1821
72	14.3568	14.8610	14.8614	——
73	12.1416	12.6071	12.6069	——
74	10.3347	10.9876	10.9879	——

The residues left after the heating were always found to dissolve completely in water, forming perfectly clear solutions. A few rough determinations of sulphuric acid by precipitation as barium sulphate, were made as a further assurance that this time the compound was really anhydrous normal salt. The values found were a few tenths of a percent lower than that calculated by the formula $MnSO_4$, but did not diverge sufficiently from this to be of any consequence. From the above data it is evident that the analytical method adopted here is sufficiently accurate for the purpose in hand.

From determination 58 onward, all samples were heated at 270° to 280° for one to one and one-half hours, cooled in a desiccator in stoppered flasks and weighed within an hour of the time they were removed from the air-bath. In the earlier determinations (prior to 58) the flasks were not stoppered, but were always weighed within half an hour from the time they were transferred from the air-bath to the desiccator, and successive weighings after different periods of standing in the desiccator and balance case showed that the maximum error thus introduced did not exceed a few tenths of a milligram at any time.

In order to ensure complete saturation, each mixture was stirred in the thermostat until it seemed probable that saturation was complete; a sample was drawn and the stirring then continued for some time longer and a second sample drawn. The agreement of these two samples upon analysis was found to be a safe guide in the case of all except the monohydrate. Another and more general method, of greater certainty, which was used throughout the work on the monohydrate, and often enough upon the higher hydrates to establish the validity of the previous method for them, was the approach to the same composition of two mixtures, one made up of the salt and water, and the other of the salt and supersaturated solution. The application of these may be readily seen by referring to the data given in Table IV.

In the early part of the work, experiments were made upon the solubility of one hydrate in strong solutions made up from another hydrate. For this purpose the tetrahydrate and pentahydrate were employed; but it was found to make no difference how the solutions were prepared; the point of equilibrium depended only upon the temperature and the solid phase left at the end. This is also seen in cases where the transition of one solid phase into another occurred during the period of saturation; the solubility for the form finally left, agreeing completely with that determined in the usual way. It might have been interesting to have extended these experiments more in detail to the monohydrate, as its behavior seems to differ so from the others, but as the main reason for attempting them with the tetrahydrate and pentahydrate was to furnish the assurance that the relation of the solubility of these two salts reported by Linebarger could not be explained by such phenomena, it seemed unnecessary to proceed further at present.

The tetrahydrate, pentahydrate, and heptahydrate in themselves and in their relations to one another show no noticeable peculiarities. With the monohydrate the case is somewhat different. At moderate temperatures the systems containing it as solid phase came to equilibrium with surprising slowness. Thus at 33.7° a solution made up from water and excess of monohydrate rose during the first day to a concentration of a little more than 61 parts anhydrous salt to 100 parts of water, which during the next week gradually increased by about 1 part per 100; while during the same interval a solution saturated with respect to tetrahydrate, i. e., containing about 67.4 parts anhydrous salt per 100 of water, — to which monohydrate had been added, did not decrease in concentration by more than 0.3 parts per 100.

From the general trend of the curve, it appears probable that the solution made up from the water and monohydrate comes very much nearer to representing the true solubility of the salt than the other. This accounts for the very high values obtained by Linebarger for the solubility of the monohydrate, as his method consisted in heating up a solution of known strength until precipitation began, and taking the strength of the solution as the solubility at this temperature.

Above 40° the change is somewhat more rapid, as shown by dets. Nos. 62 to 66, while above 50° approximate equilibrium is established within a period comparable with that necessary for the other hydrates. It is in this latter region that both Mulder and Linebarger place the transition point for monohydrate, while from the present work it would appear to lie most probably quite near to that from tetrahydrate to pentahydrate. On account of the extreme slowness with which the system comes to equilibrium in this region, the position of the point could not be determined directly. The solubility curve down to 41.5° may be taken with moderate certainty. The point plotted at 33.7° represents the maximum value obtained from the solutions starting with water and monohydrates, and for the reasons already given deserves much less confidence than those at higher temperatures. The same applies in a still greater degree, of course, to the value at 18°, which is only a rough approximation. Both of these last values may be best considered as lower limits.

An inspection of the accompanying curves shows that, strictly speaking, the tetrahydrate, the commonest form on the market, is to be considered as unstable at any temperature with respect to neutral solutions or at most, stable over a very limited range of temperatures.

In preparing the tetrahydrate crystals as already described, experiments were made by varying the temperature of the thermostat containing the desiccator. For over a month one solution was kept at a temperature between 28° and 35° as extreme limits, and for the greater part of the time between 29° and 31°. In all this time, nothing but well-formed crystals of tetrahydrate separated. Similar experiments were made at temperatures up to about 48° lasting for a week or more at each temperature, with the result that up to about 40° little or no monohydrate was formed. Between 40° and 50° a mixture of monohydrate and tetrahydrate was usually obtained, and above 50° monohydrate could safely be counted on.

If pentahydrate crystals and water were placed in one of the bottles of the solubility apparatus and stirred at a temperature of 40°, within an hour the larger part of them would be converted into tetrahydrate; but it was usually necessary to continue this for many hours before the next change, i. e., to monohydrate,—would set in; and it was a matter of days before it was complete.

The details of the solubility determinations are given in Table IV. The liberty has here been taken of omitting the earliest of the determinations, made before the method and apparatus were well in hand; also a number over the unstable parts of the curves where the transition to another hydrate had evidently set in, but had not been completed before the sample was drawn; and finally a number which from imperfections in the manipulation, such as too great variation in temperature during saturation, imperfect filtration in drawing sample and the like, while useful to some extent as rough checks and suggestions during the progress of the work, add nothing to the final results.

The determinations are here arranged in the order in which they were made. Usually two or three bottles containing different mixtures were placed on the wheel of the apparatus at one time, and thus the solubilities of different hydrates determined in exactly similar conditions.

The column headed "Mixture No." indicates which samples were drawn from the same bottle without other change in the contents of the latter than that caused by a longer period of saturation. Thus every time water, salt, or solution was added to a bottle, it was considered as a new mixture and has been so numbered. In the same column the sign ↓ indicates falling concentration, i. e., at the start the liquid phase consisted of a supersaturated solution and consequently salt would crystallize out as stirring continued. Similarly the sign ↑ indicates that to begin with, the liquid phase was either pure water or a solution weaker than the saturated solution for that temperature and hydrate, and consequently tended to dissolve the hydrate, the concentration rising until saturation was reached. The convergence of the results from such a pair of mixtures furnishes us with the best criterion to trace the approach of the system to equilibrium. The necessity of such a guide is clearly seen in the experiments on the monohydrate, particularly at moderate temperatures, which have been already referred to.

TABLE IV

Det. No.	Mixture No.	Hydrate used as solid phase	Temp. °C.	Time of saturation	Approx. weight of sample analyzed. Gms.	Parts $MnSO_4$ per 100 parts H_2O
[1]1	1↕	5	16.0	2.5	2.7	61.62
2	2↕	5	16.0	2	2.4	61.57
[2]3	3↓	5	16.0	2.5	2.6	61.51
4	2↕	5	16.0	2.5	2.7	61.68
5	4↕	4	16.0	2	2.6	64.01
6	4↕	4	16.0	4	2.8	63.86
7	4↕	4	16.0	6	2.1	63.94
8	5↕	5	25.0	1	2.4	64.78
9	6↕	4	25.0	1.5	3.0	65.26
10	6↕	4	25.0	2 2	2.9	65.38
11	5↕	5	25.0	2.2	2.9	64.79
12	8↕	4	30.0	2	3.0	66.42
[3]13	7↓	5	30.0	2	2.7	67.76
14	8↕	4	30.0	3.5	3.6	66.37
[4]15	7↓	4	30.0	3.5	4.0	66.49
16	9↕	4	35.0	2	3.0	67.82
[5]17	10↓	4	35.0	2	2.6	67.92
18	11↕	4	18.5	2.7	2.4	64.18
19	12↕	4	18.5	2.7	2.3	64.20
20	13↕	4	39.9	1	2.5	68.83
21	13↕	4	39.9	2.2	3.7	68.79
22	14↕	4	17.7	0.5	2.7	64.22
23	15↕	4	17.7	0.5	2.4	64.20
24	14↕	4	17.7	1.5	2.5	63.94
25	15↕	4	17.7	1.5	2.4	64.10
26	14↕	4	17.7	3.7	2.1	64.17
27	15↕	4	17.7	3.7	2.6	64.17
28	16↕	5	9.0	1.2	2.5	59.14
29	17↕	7	9.0	1.2	2.4	59.34
30	16↕	5	9.0	2	2.1	59.23
31	17↕	7	9.0	2	1.3	59.25

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[1] Started with a mixture of penta- and tetrahydrates, but transition to penta complete before sample was drawn.

[2] Mixture at first contained only tetrahydrate as solid phase, but transition to pentahydrate occurred during saturation.

[3] Probably an error in det. (See det. 69 and 70.) Not plotted.

[4] Transition to tetrahydrate has here evidently occurred.

[5] Mixture started with pentahydrate, but transition set in during saturation.

TABLE IV—(*Continued*)

Det. No.	Mixture No.	Hydrate used as solid phase	Temp. °C.	Time of saturation	Approx. weight of sample analyzed. Gms.	Parts $MnSO_4$ per 100 parts H_2O
[1]32	18	7	—10	—	2.2	47.96
33	19	5	5.0	1	2.4	58.06
34	20	7	5.0	1	2.6	56.59
[2]35	19	7	5.0	2.2	2.8	56.24
36	20	7	5.0	2.5	2.7	56.31
[3]37	21	(4)	9.0	0.7	2.3	59.31
38	20	7	9.0	1.5	2.3	59.41
[4]39	22	7	0.0	0.7	2.3	53.35
[5]40	23	7	0.0	1.5	2.5	53.18
41	24	7	0.0	1.5	2.7	53.15
42	25	5	35.5	0.3	2.6	71.61
43	26	4	35.5	0.7	2.6	68.02
44	26	4	35.5	2	2.7	68.14
45	27	4	32.2	1.7	2.5	66.82
46	27	4	32.2	3.2	2.3	66.83
47	27	4	49.9	1	1.9	72.54
48	27	4	49.9	2.5	2.4	72.42
[6]49	28	4	50.0	1	1.9	72.83
50	29	5	12.0	1.2	2.3	60.15
51	30	5	12.0	1.2	2.2	60.20
52	30	5	12.3	2.2	2.6	60.13
53	29	5	12.3	2.2	2.6	60.19
54	31	5	15.0	1.5	2.5	61.08
55	32	7	12.0	1	3.0	61.87
56	32	7	12.0	1.5	2.9	61.68
57	33	7	14.3	1	2.7	63.93
58	34	1	41.4	47.5	1.4	61.21
59	34	1	41.4	90.2	1.4	60.94
[7]60	34	1	41.6	156	1.2	61.23

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[1] Rough determination made by analyzing mother-liquor from preparation of heptahydrate.

[2] Transition from pentahydrate set in spontaneously (Cf. det. 33).

[3] Tetrahydrate evidently transformed to one of the higher hydrates.

[4] Det. started with tetrahydrate, but evidently heptahydrate formed during saturation.

[5] Det. started with pentahydrate, but evidently heptahydrate formed during saturation.

[6] Det. started with pentahydrate. Evidently transition to tetrahydrate set in.

[7] The time here includes the 90.2 hours at 41.4°.

TABLE IV—(*Continued*)

Det. No.	Mixture No.	Hydrate used as solid phase	Temp. °C.	Time of saturation	Approx. weight of sample analyzed. Gms.	Parts $MnSO_4$ per 100 parts H_2O
61	35	1	41.6	65.5	1.4	62.14
62	34	1	41.6	198.5	1.2	60.87
[1]63	35	1	41.6	119.5	1.3	60.97
[2] 64	35	1	41.7	137.5	1.4	60.82
65	35	1	41.5	167.5	1.1	60.77
66	35	1	41.5	189.5	1.0	60.59
[3]67	36	4	50.0	1	0.7	72.4
[4]68	37	1	18	(?)	1.1	68.3
[5] 69	38	5	31.1	1	1.4	67.94
70	38	5	31.1	1.5	1.9	67.90
[6]71	39	1	50.0	0	1.4	72.53
[7]72	40	1	50.0	3	1.4	58.14
[8]73	41	1	50.0	2	1.3	57.41
[9] 74	39	1	50 0	4	1.7	62.32
75	39	1	50.3	28.5	1.7	58.31
76	40	1	50.3	27.5	1.5	57.89
77	41	1	50.3	26.5	1.5	58.32
78	41	1	67.5	16.5	1.2	52.10
79	42	1	67.5	48	1.7	51.60
80	43	1	75.0	2	1.7	51.42
81	44	1	75.0	1.2	1.1	47.48
82	45	1	95.0	0.7	1.7	38.71
83	46	1	84.8	2.5	1 2	45.12
84	47	1	84.8	3	1.4	43.63
85	46	1	84.8	3.5	2.1	45.04
86	47	1	84.8	4.2	1.2	45.69
87	48	1	67.0	17.5	2.0	51.50
88	49	1	67.0	17.5	1.6	50.43
89	49	1	67.0	23	2.1	51.19
90	48	1	67.0	23.5	1.0	51.42
91	50	1	99.6	4	2.4	35.63
92	51	1	99.6	4.2	2.7	34.11
93	50	1	99.6	8.7	1.1	34.49
94	51	1	99.6	8.2	0.8	33.24

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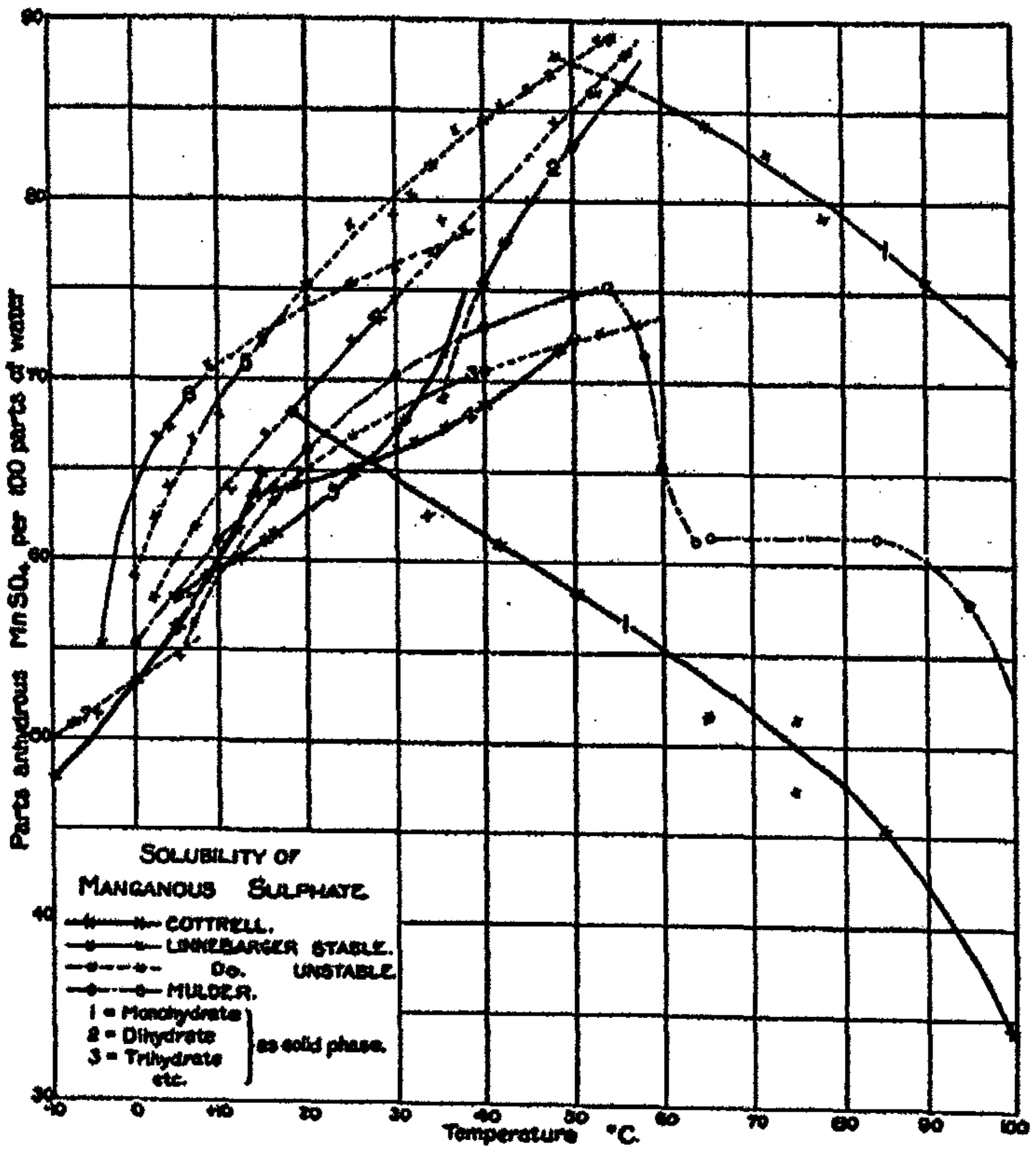
[1] The time here includes that at 41.6°.

[2] The time here includes that at 41.6° and 41.7°.

[3] Made by placing powdered pentahydrate in water and bringing up to temperature when transition sets in. Only intended as rough approximation.

[4] Started as a determination of monohydrate at 50° about 5 p.m., but

The data given in this table are also embodied in the accompanying set of curves, where for the sake of comparison have been added those of Linebarger and Mulder. In Linebarger's curves, the parts given by him as stable are represented



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gas went out during the night and bath was found next morning at 18° (motor still running) and sample taken.

[5] Taken with particular pains to verify or correct det. 13.

[6] Solution made by saturating water at 50° with tetrahydrate and then adding monohydrate and drawing sample within a few minutes.

[7] Solution made by adding monohydrate dried at 130° ± to water.

[8] Sample slightly cloudy. Solution prepared by adding freshly precipitated monohydrate, which had not been dried in oven, to water.

[9] Time here includes that at 50°.

by continuous lines and the unstable portions by dotted lines. The abscissæ represent temperature in °C and the ordinates are parts of anhydrous salt per 100 parts of water.

My warmest thanks are due to my good friends of the Chemical Department for the kindly interest and help they have extended during this work. In particular I wish to acknowledge my indebtedness to Dr. W. C. Blasdale for carrying out check analyses on a portion of the work and to Mr. G. W. Beattie, who in the early stages of the problem, kindly undertook some experiments on the electrical conductivity of solutions of the salt that had been kept at different temperatures for some time, in order to determine, if possible, whether any change in the constitution of the solution occurred. No appreciable differences were noted between solutions kept at room temperature and the same solution which had been heated for a week or more at 30° to 40°. This work was carried out before the errors in Linebarger's values were discovered, and, after these had come to light, the explanation of the phenomena naturally took an easier channel and the resistance measurements were discontinued.

The main results of the present paper may be summed up as follows:

1. The solubility of the hydrates of manganous sulphate with 1, 4, 5, and 7 molecules of water of crystallization have been determined for temperatures between −10° and +100° C.

2. Contrary to the results of Linebarger, there appears to be nothing peculiar in the behavior of the last three, but systems containing the monohydrate as solid phase reach equilibrium very slowly, this effect being greatest at the lower temperatures.

3. The temperature of 170° C is not sufficient to expel the last molecule of water from manganous sulphate as assumed by Linebarger and his results are consequently too high.

4. A temperature of 250° is sufficient to dehydrate manganous sulphate completely, and there is no appreciable decomposition of the anhydrous salt up to temperatures considerably above 300°.

5. In the case of the three higher hydrates at least it makes

no difference from which of them the solution is prepared; at a given temperature if it is finally saturated with either one of the hydrates, its concentration will depend only upon this latter.

6. Incidentally, a few simple devices which have been found of use in the solubility determinations have been described.

University of California,
June, 1900.

CATALYSIS AND CHEMICAL ENERGY

BY OSCAR LOEW

Recently an article appeared in Vol. 31 of the Zeitschrift für physikalische Chemie by G. Bredig and R. Müller von Berneck, which contained a short review of the different hypotheses in regard to the phenomenon of catalysis. This review may be completed by the following paragraphs: In the first place, the view of Ostwald[1] expressed in 1895 should be quoted: "What causes the action of catalytic substances is at present still a mystery, the solution of which is the more difficult, as it can only be found on the basis of new principles which reach beyond the laws of energy." In the second place that of the writer should be mentioned, in regard to the catalytic action of platinum black at the ordinary temperature.[2] According to this view it is the oscillations of the free heat energy of the atmosphere which are modified by certain peculiarities of the platinum atom in such a manner that they can pass still more easily than they usually do into the oscillations of chemical energy. These modified oscillations become still more powerful when the platinum black has absorbed molecular oxygen to which these modified heat oscillations are transferred. The writer has observed that platinum black charged with oxygen can cause a reduction of nitrates to ammonia in presence of glucose, and that this process stops when the molecular oxygen surrounding the platinum particles is removed or consumed by a secondary action consisting in a direct oxidation of glucose. The absorbed oxy-

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[1] Aula, Heft. 1. "Worauf die Wirkung katalytischer Stoffe beruht, is zur Zeit noch ein Raethsel, dessen Loesung um so schwieriger ist, als sie nur auf grund neuer Principien, welche über das Energiegesetz hinausgehen, gefunden werden konnte."

[2] Ber. chem. Ges. Berlin, 23, 677 (1900).

gen becomes a powerful oxidizer under the influence of these oscillations. It is still the general belief that the oxygen absorbed by the platinum black owes its efficiency merely to its denser state. If that be correct then oxygen compressed by a pump ought to behave in the same way, which is not at all the case.

The catalytic action of certain organic compounds was traced by the writer to the chemical energy of labile atoms. Thus far the relations of chemical lability to chemical energy have attracted but very little attention. Atoms in labile position are characterized by a state of lively oscillations, different from the mere heat oscillations of the atoms in stable position. Oscillations due to chemical lability may be of wider amplitude than those of heat, since the former can loosen affinities in a much more marked degree at the ordinary temperature than heat energy can do under the same circumstances. Since these oscillations can easily produce chemical changes in certain other compounds they must be defined as chemical energy.

Chemical energy can occur associated with organic compounds in a potential and in a kinetic form. A kinetically labile compound is characterized on the one hand by the easy change to a more stable isomeric or polymeric modification or compound, and on the other by the great facility with which it enters into reaction with various other compounds, especially such as also possess labile properties and thus products result with a lesser degree of instability. Potentially labile compounds behave differently, they do not pass into isomeric or polymeric modifications and they do not easily yield various derivatives, but are inclined to sudden and far-reaching decomposition or explosion. Examples of the former class are aldehydes, ketones, amidoaldehydes, amidoketones; of the latter class the diazo compounds and the nitrates of polyvalent alcohols, as nitroglycerol.

This intramolecular potential chemical energy is to be clearly distinguished from the potential chemical energy of all organic compounds, illustrated by the process of combustion.

Free chemical energy in a labile compound is caused by a loose position of atoms in certain atomic groups and this loose position is the consequence of a depression of affinities on account of one atom being under the simultaneous influence of two neighboring atoms.

Such labile atoms are subjected to much more violent oscillations under the influence of heat energy than are the other atoms in stable position in the same compound, and thus heat energy can easily pass into chemical energy through the agency of labile atomic groups. As the writer has pointed out repeatedly, the living matter and the enzymes furnish the most striking examples for this theorem. The reader may be referred to recent articles of the writer in "Science," December, 1899, and June, 1900: On the Chemical Nature of Enzymes, and On the Proteids of Living Matter. Those who are more particularly interested in this line may be referred to the work of the writer: Die chemische Energie der lebenden Zellen, Chapters 5 and 11. Munich, 1899: E. Wolff, publisher. In this treatise the chemical energy associated with aldehyde groups is treated in detail.

P. S. — After this was written an article of Hans Euler[1] came to the writer's notice in which the catalytic action of platinum black upon hydrogen peroxide was in part attributed to the oxygen condensed upon the metallic particles. He observed a very great difference in the intensity of action at the beginning of the reaction between the freshly reduced platinum black and that which had been exposed to air. Euler seems not aware that the writer, ten years before he did, drew the same inference[2] as to the essential influence of the absorbed oxygen upon catalytic processes, even on some that are by no means simple oxidations, as the reaction between nitrates and glucose above mentioned.

Division of Vegetable Physiology,
U S. Dept. of Agriculture,
Washington, D. C.,
July, 1900.

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[1] Chem. Zeitung, Aug. 4, 1900. Extract from "Öfversigt af Kgl. Vetensk. Akad." Förhandl. 2, 267 (1900).

[2] Ber. chem. Ges. Berlin, 23, 677 (1900).

THE REACTION BETWEEN CHLOROFORM AND POTASSIUM HYDROXIDE

BY A. P. SAUNDERS

This reaction is generally represented in the textbooks by the equation:

$$CHCl_3 + 4KOH = 3KCl + 2H_2O + CHO_2K.$$

According to this the reaction might involve primarily three molecules of potassium hydroxide and one of chloroform, to give potassium chloride and formic acid, the last being then at once neutralized by another molecule of potash; or it might be pentamolecular from the start, one molecule of chloroform reacting at once with four molecules of potash; or, finally, it might go in stages, each one of which is bimolecular, consisting of successive replacements of chlorine in the chloroform molecule.

The object of the present investigation was to determine, if possible, the order of this reaction. The case is complicated by the fact that potassium formate is unstable and breaks down partially to carbon monoxide and potash;[1] thus the concentration changes are here subject to varying influences, the exact nature of which is not as yet understood.

The experiments recorded below were carried out in the following manner: From ordinary 95 percent alcohol, a solution of alcoholic potash was prepared, of known strength. The alcohol, when tested as to its neutrality, was found to be faintly acid; the error introduced in this way in those cases where alcohol was used as a diluent was not large enough to affect the results in any sensible degree. A solution of chloroform of equivalent concentration was also made in alcohol, reckoning three

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[1] Geuther. Liebig's Ann. 123, 121 (1862).

molecules of potash to one of chloroform; i. e., the chloroform solution was one-third as concentrated as the potash solution when calculated in gram-equivalents per liter. Owing to the partial and variable decomposition of the formate it is impossible to prepare solutions which shall remain equivalent after the reaction has begun, because there is no constant ratio between the change of concentration of potash and that of chloroform.

The solutions so prepared were placed in an Ostwald thermostat and, after a sufficient time had elapsed, were mixed in the desired proportions in separate small flasks, standing in the same bath; these were then removed at stated intervals, immediately cooled under a tap, made up with water to a certain volume, and analyzed. The alkalinity was determined by titrating against a hydrochloric acid solution, using phenol phthalein, and chlorine was determined by silver nitrate against ammonium sulphocyanate. All the measuring vessels employed were previously calibrated.

The series are as follows:

SERIES I

Temperature	44.5° corr.
Alcoholic potash	0.482 N.
Chloroform	0.1625 gr. equiv. per liter.

The separate reaction solutions were made by mixing 25 cc of alcoholic potash with an equal volume of chloroform solution; their initial concentrations were therefore one-half of the above.

The values recorded in the table below are as follows:

1. Arbitrary numbers of the experiments.
2. Interval of time in minutes between each experiment and the succeeding one (Δt).
3. Concentration of potassium chloride in the mixture (initial conc. 0.0).
4. Concentration of potassium hydroxide in the mixture (initial conc. 0.241).
5. Total change in conc. of potash from the initial conc.

6. Actual concentration of potassium as formate; i. e., the difference between the values of 5 and 3.

7. Calculated concentration of potassium as formate; i. e., one-third of the values in 3.

8. Percent of undecomposed formate; i. e., 6 divided by 7.

9. Change of conc. of potassium chloride (by intervals) (Δx).

10. Change per minute $\left(\frac{\Delta x}{\Delta t}\right)$.

11. Mean concentrations of potash (c_1) calculated from 4, by taking the mean of each value and the preceding one.

12. Concentration of chloroform, calculated by deducting the values of 7 from the initial concentration of chloroform 0.0812.

13. Mean concentration of chloroform (c_2) by taking the mean of each value and the preceding one.

14. $K = \frac{\frac{\Delta x}{\Delta t}}{c_1 c_2} \cdot 10^4$. (Assuming the reaction to be bimolecular.)

15. $K = \frac{\frac{\Delta x}{\Delta t}}{c_1^3 c_2} \cdot 10^2$. (Assuming the reaction to be tetramolecular.)

SERIES I

1	No. of exp.	10	1	4	11	2
2	Time intervals (Δt)	20	30	26	24	23
3	Conc. of KCl	0.0256	0.0535	0.0737	0.0839	0.0942
4	Conc. of KOH (0.2410)	0.2055	0.1741	0.1505	0.1388	0.1252
5	Change of conc. of KOH	0.0355	0.0669	0.0905	0.1022	0.1158
6	Conc. of K as formate	0.0099	0.0134	0.0168	0.0183	0.0216
7	The same calc. as 1/3 of 3	0.0085	0.0178	0.0246	0.0279	0.0314
8	Percent undecomposed formate	116.5	75.3	68.4	65.1	70.0
9	Change of conc. of KCl (Δx)	0.0256	0.0279	0.0202	0.0102	0.0103
10	Change per minute $\left(\frac{\Delta x}{\Delta t}\right)$	0.00128	0.00093	0.000777	0.000425	0.000448
11	Mean conc. of KOH (c_1)	0.2232	0.1898	0.1623	0.1446	0.1320
12	Conc. of $CHCl_3$ (0.0812)	0.0727	0.0632	0.0566	0.0533	0.0498
13	Mean conc. of $CHCl_3$(c_2)	0.07695	0.06795	0.05990	0.05495	0.05155
14.	$K = \frac{\frac{\Delta x}{\Delta t}}{c_1 c_2} \cdot 10^4$	747	722	800	536	660
15	$K = \frac{\frac{\Delta x}{\Delta t}}{c_1^2 c_2} \cdot 10^2$	150	200	304	256	379

SERIES II

The results of this series and of those which follow are recorded in the same way as the above.

Temperature	44.5° corr.
Alcoholic potash	0.482 N.
Chloroform	0.1625 gr. equiv. per liter.

The separate reaction solutions were made up by adding 25 cc of alcoholic potash to 25 cc of chloroform solution, and then diluting with 50 cc of alcohol. The solutions therefore contained

0.1205 gr. equiv. KOH, and 0.0406 gr. equiv. $CHCl_3$ per liter.

If the reaction proceeds as a bimolecular one, then by halving the concentration of both the reacting substances, we should find that the decomposition goes on one-fourth as fast in the more dilute solution as in the more concentrated one; whereas if the reaction is tetramolecular, it should go on one-sixteenth as fast. Plainly the former is much nearer the truth than the latter; and the first values are fairly correct for the former assumption. But the solutions which begin with the concentrations in the proportion of two to one, soon depart from this ratio. We can calculate from the velocity in Series I. what the velocity in Series II. should be at any time, by taking, not one-fourth of $\frac{\Delta x}{\Delta t}$ in Series I, but that fraction which corresponds to the concentrations themselves. Thus if we call $c_1^{(1)}$ the concentration of potash in the first series, $c_2^{(1)}$ that of chloroform; and for the second series, $c_1^{(2)}$ and $c_2^{(2)}$, we can calculate at each point, from the value of $\frac{\Delta x}{\Delta t}$ in Series I., and the values of $c_1^{(1)}$, $c_2^{(1)}$, $c_1^{(2)}$, $c_2^{(2)}$, what value $\frac{\Delta x}{\Delta t}$ should have in Series II., by using the formula

$$\frac{\Delta x^{(1)}}{\Delta t}\cdot\frac{c_1^{(2)}c_2^{(2)}}{c_1^{(1)}c_2^{(1)}}=\frac{\Delta x^{(2)}}{\Delta t}.$$

These calculations yield the results:

SERIES II

1	No. of exp.	6	5	3	15	7
2	Time intervals (Δt)	20	30	26	24	23
3	Conc. of KCl	0.00595	0.01277	0.01833	0.02230	0.02660
4	Conc. of KOH (0.1205)	0.1082	0.1007	0.0938	0.0893	0.0850
5	Change of conc. of KOH	0.0123	0.0198	0.0267	0.0312	0.0355
6	Conc. of K as formate	0.0063	0.0070	0.0084	0.0089	0.0089
7	The same calc. as 1/3 of 3	0.0019	0.0044	0.0061	0.0074	0.0089
8	Percent undecomposed formate	326	160	137	120	100
9	Change of conc. of KCl (Δx)	0.00595	0.00682	0.00556	0.00397	0.0043
10	Change per minute $\left(\frac{\Delta x}{\Delta t}\right)$	0.000297	0.000227	0.000214	0.000165	0.000187
11	Mean conc. of KOH (c_1)	0.1144	0.1045	0.0973	0.0916	0.0872
12	Conc. of $CHCl_3$ (0.0406)	0.0387	0.0362	0.0345	0.0332	0.0317
13	Mean conc. of $CHCl_3$ (c_2)	0.0396	0.0374	0.0353	0.0338	0.0324
14	$K = \dfrac{\frac{\Delta x}{\Delta t}}{c_1 c_2} \cdot 10^4$	656	582	623	533	662
15	$K = \dfrac{\frac{\Delta x}{\Delta t}}{c_1^3 c_2} \cdot 10^2$	501	533	658	637	872

No. of expt.	6	5	3	15	7
$\frac{\Delta x^{(2)}}{\Delta t}$ Calc.	0.000338	0.000282	0.000275	0.000166	0.000186
Found	0.000297	0.000227	0.000214	0.000165	0.000187

SERIES III

In this and the following series the concentration of chloroform was made practically constant by using in each reaction mixture 25 cc of pure chloroform. These solutions were diluted with water to 250 cc for analysis; on diluting, the chloroform separates out as a heavier layer, but it was found that the potassium hydroxide and chloride were practically confined to the water layer; hence a correction was merely made for the volume of the chloroform layer, and it was not further taken into account.

Because of the high concentration of chloroform, the reaction goes on much more rapidly than in the preceding series, and it was accordingly found convenient to work at lower temperatures.

SERIES III

Temperature	21.5° corr.
Alcoholic potash	0.482 N.

The separate reaction solutions made up by adding 25 cc of alcoholic potash to 25 cc of pure chloroform; they therefore contained

0.2410 gr. equiv. of KOH,

and were of practically constant concentration with respect to chloroform; hence the values recorded under 12 and 13 in the preceding tables, are omitted here.

SERIES IV

Temperature	21.5° corr.

Reacting solutions made by adding 25 cc alcoholic potash (0.482 N) to 25 cc pure chloroform, and then diluting with 50 cc alcohol; they therefore contained

0.1205 gr. equiv. of KOH,

and the concentration of chloroform was constant.

SERIES III

1	No. of exp.	1	3	5	7	11
2	Time intervals (Δt)	21	22	24	23	60
3	Conc. of KCl	0.0668	0.1030	0.1338	0.1500	0.1780
4	Conc. of KOH (0.241)	0.174	0.135	0.103	0.0822	0.0531
5	Change of conc. of KOH	0.067	0.106	0.138	0.1588	0.1879
6	Conc. of K as formate	0.00	0.00	0.0018	0.006	0.0073
7	The same calc. as 1/3 of 3	0.0223	0.0343	0.0446	0.0500	0.0593
8	Percent undecomposed formate	0	0	3.9	11.8	12.2
9	Change of conc. of KCl (x)	0.0668	0.0362	0.0308	0.0162	0.0280
10	Change per minute $\left(\frac{\Delta x}{\Delta t}\right)$	0.00318	0.00165	0.00128	0.00071	0.00047
11	Mean conc. of KOH (c_1)	0.2075	0.1545	0.119	0.0926	0.0676
14	$K = \frac{\frac{\Delta x}{\Delta t}}{c_1}$	153	107	107	76	69
15	$K = \frac{\frac{\Delta x}{\Delta t}}{c_1^3}$	355	450	760	887	1500

SERIES IV

1	No. of exp.	2	4	6	10	15
2	Time intervals (Δt)	21	22	24	23	60
3	Conc. of KCl	0.01805	0.0323	0.0423	0.0520	0.0710
4	Conc. of KOH (0.1205)	0.1012	0.0868	0.0742	0.0625	0.0433
5	Change of conc. of KOH	0.0193	0.0337	0.0463	0.0580	0.0772
6	Conc. of K as formate	0.00135	0.0014	0.0040	0.0060	0.0062
7	The same calc. as 1/3 of 3	0.00602	0.0108	0.0141	0.0173	0.0237
8	Percent undecomposed formate	22.4	13.0	28.4	34.6	26.2
9	Change of conc. of KCl (Δx)	0.01805	0.01425	0.0100	0.0097	0.019
10	Change per minute $\left(\frac{\Delta x}{\Delta t}\right)$	0.000860	0.000648	0.000417	0.000422	0.000316
11	Mean conc. of KOH (c_1)	0.1108	0.0940	0.0805	0.0683	0.0531
14	$K = \frac{\frac{\Delta x}{\Delta t}}{c_1} . 10^5$	767	690	518	617	595
15	$K = \frac{\frac{\Delta x}{\Delta t}}{c_1^3} . 10^3$	625	780	800	1320	2110
16	$\frac{\Delta x}{\Delta t}$ compared with Series III	$\frac{1}{2.7}$	$\frac{1}{3.9}$	$\frac{1}{3.2}$	$\frac{1}{6.0}$	$\frac{1}{6.8}$

Making the same calculation that was made for the other series, i. e., from the relative concentration of potash at each point, calculating the reaction velocity for Series IV. from Series III. allowing for the fact that the chloroform was uniformly one-half as concentrated, we find for $\frac{\Delta x}{\Delta t}$ in Series IV:

	2	4	6	10	15
Calc.	0.000850	0.000500	0.000443	0.000260	0.000184
Found	0.000860	0.000648	0.000417	0.000422	0.000316

The agreement here between the results found and those obtained by calculation is by no means as good as in the other case, but it is at least near enough to indicate that the reaction velocity is proportional to the concentration of the potash rather than to the third power of that value.

That these results in general should vary considerably from those calculated for any given formula does not appear surprising when we look over the values for the undecomposed formate and see how much they vary. I tabulate here again for convenience those percentages and the corresponding original composition of the solutions.

I	25 cc KOH in alcohol 25 cc $CHCl_3$ in alcohol	116.5	75.3	68.4	65.1	70.0
II	25 cc KOH in alcohol 25 cc $CHCl_3$ in alcohol 50 cc alcohol	326	160	137	120	100
III	25 cc KOH in alcohol 25 cc pure $CHCl_3$	0.0	0.0	3.9	11.8	12.2
IV	25 cc KOH in alcohol 25 cc pure $CHCl_3$ 50 cc alcohol	22.4	13.0	28.4	34.6	26.2

It will be understood that these percentages are not quantitatively accurate; it did not lie within the scope of this investigation to obtain results of extreme accuracy; rather to find in general the nature of the changes which go on.

Comparisons can only be made independently between Series

I. and II., and Series III. and IV., because the temperature was lower for the latter pair; but it is plain that dilution with alcohol tends to prevent the decomposition of the formate. Furthermore, Series II. shows that there is in that case a formation of some other substance than formic acid, probably some of the intermediate compounds between chloroform and orthoformic acid, or even, in the earlier stages of the reaction, potassium orthoformate itself. In this connection it is worth while to call attention to the experiments of Williamson and Kay,[1] who found that sodium ethylate and chloroform yielded ethyl orthoformate. The results of Series II. indicate that, if such a formation of potassium orthoformate actually takes place, it does not remain in the solution, but is decomposed as the reaction proceeds.

A reaction velocity constant can hardly be deduced from these results. In view of the wide variation in each series, it was not considered worth while to attempt to apply a complex and tedious integration. The Series I. and II. indicate a value lying perhaps between 600 and 700, and they show at least, clearly, that the tetramolecular formula gives values which vary much more widely than those obtained with the bimolecular formula.

Among the disturbing factors, we have to consider, besides the irregularities, arising from the formation of potassium formate, the separation of potassium chloride in crystalline form, which begins very early in the history of the change; there may in some cases be a separation of potassium formate as well, out of the solution. The formation of water produced by the reaction would also affect the reaction velocity in one way or the other; Dumas[2] states that an aqueous solution of caustic potash has no action on chloroform, even when boiled with it; from this it would seem probable that the presence of water in an alcoholic solution would retard the reaction; and we might therefore expect that the constantly increasing amount of water in the experiments here described would lead to a corresponding decrease in the re-

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[1] Mem. Chem. Soc. 7, 224.

[2] Ann. Phys. Chim. (2) 56, 115 (1834).

SERIES V

1	No. of exp.	2	6	9	11	12	10	8
2	Time intervals (Δt)	0	15	25	99	47	54	80
3	Conc. of KCl	0.0022	0.0151	0.0316	0.0770	0.0865	0.0987	0.1097
4	Conc. of KOH (0.2885)	0.283	0.268	0.247	0.1895	0.1785	0.160	0.149
5	Change of conc. of KOH	0.0	0.015	0.036	0.0935	0.1045	0.123	0.134
6	Conc. of K as formate	−0.0022	0.00	0.0044	0.0165	0.0180	0.0243	0.0243
7	The same calc. as 1/3 of 3	0.0007	0.005	0.0105	0.0256	0.0288	0.0329	0.0366
8	Percent undecomposed formate	—	0	42	64.5	62.5	74	66.5
9	Change of conc. of KCl (Δx)	—	0.0129	0.0165	0.0454	0.0095	0.0122	0.0110
10	Change per minute $\left(\frac{\Delta x}{\Delta t}\right)$	—	0.00086	0.00066	0.00046	0.000202	0.000226	0.000137
11	Mean conc. of KOH (c_1)	—	0.275	0.257	0.218	0.184	0.169	0.154
12	Conc. of $CHCl_3$	0.0525	0.0475	0.0420	0.0269	0.0237	0.0196	0.0159
13	Mean conc. of $CHCl_3$ (c_2)	—	0.0500	0.0447	0.0344	0.0253	0.0216	0.0177
14	$K = \frac{\frac{\Delta x}{\Delta t}}{c_1 c_2}$	—	625	575	613	435	620	503
15	$K = \frac{\frac{\Delta x}{\Delta t}}{c_1^3 c_2}$	—	827	870	1290	1280	2180	2120

Series VI

1	No. of exp.	12	9	1	4
2	Time intervals (Δt)	40	41	115	189
3	Conc. of KCl	0.0475	0.0743	0.1293	0.1615
4	Conc. of KOH (0.2885)	0.232	0.200	0.133	0.0927
5	Change of conc. of KOH	0.056	0.088	0.155	0.1953
6	Conc. of K as formate	0.0085	0.0137	0.0257	0.0338
7	The same calc. as 1/3 of 3	0.0158	0.0248	0.0431	0.0538
8	Percent undecomposed formate	53.8	55.2	59.7	62.7
9	Change of conc. of KCl (Δx)	0.0475	0.0268	0.0550	0.0322
10	Change per minute $\left(\frac{\Delta x}{\Delta t}\right)$	0.00119	0.000653	0.000478	0.000170
11	Mean conc. of KOH (c_1)	0.260	0.216	0.1665	0.1128
12	Conc. of $CHCl_3$ (0.0850)	0.0692	0.0602	0.0419	0.0312
13	Mean conc. of $CHCl_3$ (c_2)	0.0771	0.0647	0.0510	0.0365
14	$K = \frac{\frac{\Delta x}{\Delta t}}{c_1 c_2}$	594	468	568	413
15	$K = \frac{\frac{\Delta x}{\Delta t}}{c_1^2 c_2}$	880	1003	1870	3240

action-velocity constant; on the other hand, the amount of water present in the alcohol to begin with was so large that the changes produced in this way would be relatively trifling.

SERIES V

Temperature	43.5° corr.
Alcoholic potash	0.577 N.
Chloroform	0 105 gr. equiv. per liter.

The separate reaction solutions were made up by adding 25 cc of alcoholic potash to 25 cc of chloroform solution; they therefore had a concentration of 0.2885 gr. equiv. of potash and 0.0525 gr. equiv. of chloroform per liter. One analysis was made immediately, to ascertain the initial concentration.

SERIES VI

Temperature	43.5° corr.
Alcoholic potash	0.577 N.
Chloroform	0.170 gr. equiv per liter.

The separate reaction solutions were made up by adding 25 cc of alcoholic potash to 25 cc of chloroform solution; they had a concentration of 0.2885 gr. equiv. of potash and 0.0850 gr. equiv. of chloroform per liter.

While the variations in the reaction-velocity constant calculated from the bimolecular formula are a good deal larger than one would wish, it is plain that they are quite irregular, at least in most of the series; and the results obtained from this formula are in all cases much better than those which come out for the tetramolecular formula; probably a more exact study of the reaction under better conditions would yield a satisfactory constant.

CONCLUSION

The present investigation shows that in all probability the reaction between chloroform and potassium hydroxide proceeds in stages, in each of which only two molecules react together.

The experimental part of the investigation was carried on at Cornell University, in the laboratory of Professor Bancroft, to whom I am indebted for his friendly interest and useful suggestions.

Hamilton College, Clinton,
Sept., 1900.

VAPOR-PRESSURE RELATIONS IN MIXTURES OF TWO LIQUIDS, III

BY A. ERNEST TAYLOR

After obtaining the numerical results of my last paper, it is interesting to see what of theoretical interest they may contain.[1] We expect to find some relation between the composition of the vapor given off and the composition of the solution giving off such vapor. We also expect to find some relation between the partial pressure of acetone in the vapor and the percentage of acetone in the solution or between the partial pressure of the acetone and the pressure of pure acetone at that temperature. The most natural thing to do is to test the Law of Henry and the van 't Hoff-Raoult formula to see if they hold.[2]

The Law of Henry is formulated as follows:

$$\frac{p_1}{c_1} = \text{const.} \tag{I.}$$

or

$$\frac{p_2}{c_2} = \text{const.} \tag{II.}$$

In Equation I., p_1 is the partial pressure of the acetone in the vapor, and c_1 the corresponding concentration of the acetone in the solution. In Equation II., p_2 is the partial pressure of the water-vapor, and c_2 the concentration of the water in the solution. These equations hold at constant temperature. They are both formulations of the same law. In Equation I. acetone is the solvent and in Equation II. water. This simple formation of Henry's law would hold only when in the solution the com-

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[1] Jour. Phys. Chem. 4, 355 (1900).

[2] Margules; Wien. Ber. 104, 1243 (1895); Lehfeldt. Phil. Mag. [5] 46, 46 (1898), 48, 215 (1899).

pounds under consideration were monomolecular. That acetone exists as simple molecules in aqueous solutions, at least up to concentrations of 30 percent acetone, was shown by the freezing-point measurements of Waddell.[1]

Equations III. and IV. represent the familiar van 't Hoff-Raoult formula

$$\log_{nat}\frac{p_0}{p_1} = \frac{c_2}{c_1} = \frac{n}{N} \qquad \text{(III.)}$$

$$\log_{nat}\frac{p_0}{p_2} = \frac{c_1}{c_2} = \frac{N}{n} \qquad \text{(IV.)}$$

The letters p_1, p_2, c_1, c_2, have the same meaning as before. The vapor-pressure of pure acetone is indicated by p_2 and of pure water by p_0. N and n represent the relative number of molecules of water and acetone in the solution. By transposing and changing to ordinary logarithms, we get expressions for p_2 and p_1. These relations are more useful in the present consideration, and are given in Equations V. and VI.

$$\log_{10} p_0 - \left(0.4343\,\frac{c_1}{c_2}\right) = \log p_2. \qquad \text{(V.)}$$

$$\log_{10} p - \left(0.4343\,\frac{c_2}{c_1}\right) = \log p_1. \qquad \text{(VI.)}$$

As before, the temperature is supposed to be constant, so a set of tables, Table II.–IX. have been made out at constant temperatures from 60°–25° to test Formula V. and Table X. for Formula VI. Table I. gives a set of general constants used throughout the other tables. In these tables the first column gives the gram percentage composition of acetone in the solution, the second the total pressure of the vapor given off, the third the molecular percentage composition of the vapor in acetone, the fourth the same calculated from the formula, the fifth the gram percentage composition of acetone in the solution, the sixth the same, calculated from column four, the seventh the partial pressure of the acetone, the eighth the partial pressure of the water, and the ninth the same calculated from the formula.

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[1] Jour. Phys. Chem. 3, 160 (1899).

In working out the partial pressures of the water and the acetone, it has been assumed that one simple molecular weight of water and one simple molecular weight of acetone both occupy the same volume in the gaseous form; and that in consequence, the partial pressure of each component is proportional to the molecular percentage composition of the vapor, and can be obtained by multiplying this percentage composition by the vapor-pressure of the solution. The columns labeled p_1 and p_2 were so calculated, that is by multiplying the figures in column two by those in three, the figures in column p_1 were obtained, and $p_s - p_1 = p_2$. The figures in p_2 calc, were obtained from the Formula V. and the percentage and molecular percentage composition of the vapor corresponding determined from them by the following simple formulae:

$$\frac{p_1}{p_s} = \text{acetone percentage mol. concentration of vapor.}$$

$$\left(1 - \frac{p_1}{p_s}\right) = \text{water percentage mol. concentration of vapor.}$$

$$18\frac{p_1}{p_s} = \text{D}. \quad 58\left(1 - \frac{p_1}{p_s}\right) = \text{E}.$$

$$\frac{\text{D}}{\text{D} + \text{E}} = \text{grams of acetone in 100 g. of solution.}$$

$$\frac{\text{E}}{\text{D} + \text{E}} = \text{grams of water in 100 g. of solution.}$$

It will be seen from the tables that the van 't Hoff-Raoult equation in general predicts within one or two percent the composition of the vapor given off by any given acetone solution, and this was fully as accurately as I succeeded in determining the composition of the vapor given off. The pressure relations do not agree well, for they depend on the molecular concentration, and an error of one percent on the gram concentration of the vapor introduces an error several times as large in the molecular concentration. This is due to the fact that the molecular weights of water and acetone are so very different, viz., 18 and 58. Ninety percent acetone contains only seventy-six molecular weights of acetone to one hundred of solution, the difference between the two being particularly great at the concentrations most used. An error of two percent in the composition of the vapor would introduce an error of nearly six percent in the vapor composition. When the vapor-pressure is 700 mm this would introduce an error of 42 mm in the partial pressure of the water or of the acetone. The partial pressure of the water is not more than 100 mm, so an immense percentage error is introduced.[1]

It will be seen that there is seldom more than one percent variation between the calculated and the observed vapor decomposition up to sixty percent, after that a little more, and in the ninety percent about three percent difference. This is, I think, well beyond the possible experimental error. It can then well be said that the van 't Hoff-Raoult formula predicts accurately the composition up to sixty percent or perhaps a little higher, and above that there is a tendency for less acetone to be given off than the formula would indicate. This is exactly what one would expect from the formula and where the water acts as solvent. The tables at the lower temperatures do not give quite as good results as the higher ones, as would be expected.

Table X. shows very clearly that Formula VI. does not hold at all, where the acetone is looked upon as solvent.

Tables XI.–XVIII. contain data with reference to Henry's law as expressed in Equations I. and II. The concentrations are all molecular concentrations except in Table XII. The headings of the columns make their meaning sufficiently evident without further explanation. At 55° in Table XII. the law is tested in a variety of ways. In the fourth column gram concentrations in the solution are used. When the partial pressure of the water is considered $\frac{p_1}{c_1}$ percent has a constantly rising value; if this is changed to molecular concentrations a reasonably good constant is obtained for the lower percentages, and by taking the square root of the concentrations for the higher concentrations. This was also carried on to the cube root and a constant nearly

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[1] The apparent increase in the partial pressure of the water on dilution is further evidence of the experimental error.

as good obtained. On plotting the logarithmic curve, however, the points lie better on the square root curve.

The same methods were employed with p_1 the partial pressure of the acetone $\frac{p_1}{c_1}$ and $\frac{p_1}{\sqrt{c_1}}$ gives very little approach at a constant, but $\frac{p_1}{\sqrt[3]{c_1}}$ gives good valves at the lower concentrations and $\frac{p_1}{\sqrt[4]{c_1}}$ at the higher concentrations.[1]

The simple formula and the square root formula is used in all the other tables for the water; and the cube root and the fourth root formula for the acetone. The water formula does not hold well for the very highest concentration of acetone, nor the acetone formula for the lowest concentrations, as might be expected.

Not very great accuracy can be expected for this application of Henry's law for the partial pressures are not accurately known, especially those of the water. A more accurate knowledge of the vapor composition is needed before a satisfactory test of the law is made. It is especially unfortunate that the molecular weights of acetone and water are so different, this complicating this part of the work. The fact that the vapor from a rather dilute solution is so rich in acetone makes the accurate determination of the vapor composition almost impossible with any method yet devised. The present data would indicate however that Henry's Law does hold when complex molecules are asassumed for both the water and the acetone in solution.

This paper, then, would seem to indicate that:

The van 't Hoff-Raoult formula, when water is the solvent, predicts, within the limits of experimental error, the composition of the vapor given off from all but the highest concentrations of acetone; and that Henry's law holds only when complex molecular structure is assumed for water and acetone in solution.

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[1] Strictly speaking, the values of c_1 should be recalculated since they are based on the assumption of identity between formula weight and molecular weight; but it seemed hardly worth while to do this with the present data which are in no sense final.

TABLE I

% Ac.	C_1	Log C_1	C_2	Log C_2	$\frac{C_1}{C_2}$	$\frac{C_2}{C_1}$	$(0.4343\frac{C_1}{C_2})$	$(0.4343\frac{C_2}{C_1})$
0	0.	——	100	2.0000	——	——	——	——
10	3.3	0.5185	96.7	1.9854	0.0341	29.3	0.0148	12.73
20	7.2	0.8573	92.8	1.9675	0.0775	12.9	0.0337	5.598
30	11.7	1.0682	88.3	1.9460	0.132	7.55	0.0575	3.278
40	17.1	1.2330	82.9	1.9186	0.206	4.85	0.0896	2.106
50	23.7	1.3747	76.3	1.8825	0.310	3.22	0.1349	1.398
60	31.8	1.5024	68.2	1.8338	0.466	2.14	0.2025	0.9316
70	42.0	1.6232	58.0	1.7634	0.724	1.38	0.3145	0.5958
80	55.4	1.7435	44.6	1.6493	1.24	0.805	0.5395	0.3496
90	73.6	1.8669	26.4	1.4216	2.79	0.359	1.211	0.1558
100	100	2.0000	0.0					

TABLE II

60°

log 149 = 2.1732

% Ac.	p_s mm.	Mols. Ac vapor	Ibid. calc.	% Ac. vapor	Ibid. calc.	p_1 mm.	p_2 mm.	p_2 calc. mm.
0	149	0	0	0	0	0	149	149
10	339	56.0	57.5	80.8	81.5	190	149	144
20	485	70.5	71.5	88.5	89	342	143	138
30	577	76.8	77.5	91.5	91.8	443	134	131
40	640	77.3	81	91.8	93.3	495	145	121
50	682	81.2	84	93.3	94.5	553	129	109
60	714	82.3	87	93.8	95.5	588	126	93.5
70	740	84.3	90.3	94.5	96.8	624	116	72
80	774	86.8	94.5	95.5	98	672	102	43
90	808	88.0	99	96	99.5	711	97	9.2
100	860	100	100	100	100	860	0	0

TABLE III

55°

log 117.5 = 2.0700

% Ac.	p_s mm.	Mols Ac. vapor	Ibid. calc.	% Ac. vapor	Ibid. calc.	p_1 mm.	p_2 mm.	p_2 calc. mm.
0	117.5	0	0	0	0	0	117.5	117.5
10	275	57	58.7	81	82.2	157	118	113.5
20	399	71.5	72.8	89.0	89.5	283.5	115.5	109
30	478	77.3	78.5	91.8	92.3	370.5	107.5	103
40	534	78.7	82	92.3	93.8	420	114	95.5
50	572	82.5	85	93.8	94.8	472	100	86
60	598	83	87.7	94	95.8	496.5	101.5	73.7
70	621	85	90.8	94.8	97	528	93	57.0
80	645	87.5	94.8	95.8	98.3	566.5	78.5	34.0
90	680	89	99	96.3	99.5	602	78	7.2
100	721	100	100	100	100	721	0	0

TABLE IV

50°

log 92 = 1.9638

% Ac.	p_s mm.	Mols Ac. vapor	Ibid. calc.	% Ac. vapor	Ibid. calc.	p_1 mm.	p_2 mm.	p_2 calc. mm.
0	92	0	0	0	0	0	92	92
10	221	57	59.8	81	82.8	126	95	89
20	324	71.8	73.7	89.3	90	232.5	91.5	85
30	393	78	79.5	92	92.5	306.5	86.5	80.5
40	442	79.3	83	92.5	94	350.5	91.5	75
50	472	83	85.7	94	95	392	80	67.5
60	499	83	88.5	94	96	414	85	58
70	517.5	85.5	91.3	95	97	442.5	75	44.5
80	536	89	95	96.3	98.5	477	59	26.5
90	566.5	89.8	99	96.5	99.8	509	57.5	5.7
100	607	100	100	100	100	607	0	0

TABLE V

45°

log 71.5 = 1.8543

% Ac.	p_t mm.	Mols. Ac vapor	Ibid. calc.	% Ac. vapor	Ibid. calc.	p_1 mm.	p_2 mm.	p_2 calc. mm.
0	71.5	0	0	0	0	0	71.5	71.5
10	177	57	61	81	83.5	101	76	69
20	262	72.5	74.8	89.5	90.5	192.5	69.5	66
30	319	79.3	81.3	92.5	93.3	253	66	62.5
40	364	80.5	84	93	94.3	293	71	58
50	391	84.3	86.5	94.5	95.5	329.5	61.5	52.5
60	414	83.7	89.2	94.3	96.3	346.5	67.5	45
70	428	86.3	92	95.5	97.3	369	59	34.5
80	447	89.5	95.5	96.5	98.5	400	47	20.5
90	469	90.3	99	96.8	99.7	423.5	45.5	4.4
100	505	100	100	100	100	505	0	0

TABLE VI

40°

log 55 = 1.7404

% Ac.	p_t mm.	Mols. Ac vapor	Ibid. calc.	% Ac. vapor	Ibid. calc.	p_1 mm.	p_2 mm.	p_2 calc. mm.
0	55	0	0	0	0	0	55	55
10	139	57.5	61.8	81.3	84	80	59	53
20	209	73	76.7	89.8	91.5	152.5	56.5	51
30	258	79.8	81.3	92.8	93.3	206	52	48
40	298.5	81.2	84.7	93.3	94.7	242.5	55.5	46
50	319	85	87.3	94.8	95.7	271	48	40.5
60	340	84.3	89.8	94.5	96.5	286.5	53.5	34.5
70	352	86.8	92.5	95.5	97.5	305	47	26.5
80	368	90.3	95.7	96.8	98.7	332.5	35.5	16
90	387.5	90.3	99.2	96.8	99.7	350	37.5	3.5
100	416	100	100	100	100	416	0	0

TABLE VII

35°

log 42 = 1.6232

% Ac.	p_s mm.	Mols. Ac vapor	Ibid. calc.	% Ac. vapor	Ibid. calc.	p_1 mm.	p_2 mm.	p_2 calc. mm.
0	42	0	0	0	0	0	42	42
10	107	57.8	62	81.5	84	62	45	40.5
20	165	73.8	76.5	90	91.3	122	43	39
30	206	80.5	82.5	93	93.7	166	40	37
40	239	82.3	85.7	93.8	95	196.5	42.5	34
50	260	86.3	88.2	95.3	96	224.5	35.5	31
60	277	84.3	90.5	94.5	96.8	233.5	43.5	26.5
70	290	87.5	93.0	95.8	97.7	254	36	20.5
80	301	91.7	96	97.3	98.8	276	25	12
90	318	91.7	99.2	97.3	99.8	292	26	2.5
100	343	100	100	100	100	343	0	0

TABLE VIII

30°

log 31.5 = 1.4983

% Ac	p_s mm.	Mols. Ac vapor	Ibid. calc.	% Ac. vapor	Ibid. calc.	p_1 mm.	p_2 mm.	p_2 calc. mm.
0	31.5	0	0	0	0	0	31.5	31.5
10	82	57.8	62.8	81.5	84.5	47.5	34.5	30.5
20	130	73.8	77.5	90	91.8	96	34	29
30	164.5	81.3	83.3	93.3	94	134	30.5	27.5
40	191.5	82.3	86.5	93.8	95.5	157.5	34	25.5
50	211	86.3	89	95.3	96.3	182	29	23
60	224	84.3	91.3	94.5	97	189	35	20
70	235	87.5	93.5	95.8	97.8	205	29.5	15
80	245	91.7	96.3	97.3	98.7	225	20	9
90	258	91.7	99.3	97.3	99.8	236.5	21.5	2
100	281	100	100	100	100	281	0	0

TABLE IX

25°

log 23.5 = 1.3711

% Ac	p mm.	Mols. Ac vapor	Ibid. calc.	% Ac. vapor	Ibid. calc.	p_1 mm.	p_2 mm.	p_2 calc. mm.
0	23.5	0	0	0	0	0	23.5	23.5
10	65	58	65	81.8	85.8	38	27	22.7
20	104	74	79	90.3	92.5	77	27	21.7
30	130	81.3	84.3	93.3	94.5	105	25	20.5
40	151	83	87.3	94	95.8	125.5	24.5	19
50	168	86.8	89.8	95.5	96.5	146	22	17
60	180	84.2	91.8	94.5	97.3	152	28	15
70	188	87.5	94	95.8	98	164.5	23.5	11 5
80	198	91.8	96.5	97.3	98.8	182	16	6.8
90	209	91.8	99.3	97.3	99.8	192	17	1.5
100	229	100	100	100	100	229	0	0

TABLE X

55°

% Ac.	p_s	Mols. Ac. vapor	Ibid. calc.	% Ac. vapor	Ibid. calc.
0	117.5	0	——	0	——
10	275	57	——	81	——
20	399	71.5	0.0_3455	89	——
30	478	77.3	0.0_379	91.8	——
40	534	78.7	1.0	92.3	——
50	572	82.5	5.0	93.8	——
60	598	83	14.0	94	34.5
70	621	85	29.2	94.8	57.2
80	645	87.5	50	95.8	76.3
90	680	89	74	96.3	90.3
100	721	100	100	100	100

TABLE XI

60°

% Ac.	c_1	c_2	p_1 mm.	p_2 mm.	$\frac{p_1}{\sqrt[3]{c_1}}$	$\frac{p_1}{\sqrt[4]{c_1}}$	$\frac{p_2}{c_2}$	$\frac{p_2}{\sqrt{c_2}}$
0	0	100	0	149	—	—	1.49	14.9
10	3.3	96.7	190	149	103.5	141	1.54	15.2
20	7.2	92.8	342	143	177	209	1.54	14.8
30	11.7	88.3	443	134	195	240	1.52	14.3
40	17.1	82.9	495	145	192	243	1.77	15.9
50	23.7	76.3	553	129	192	250	1.69	14.8
60	31.8	68.2	588	126	185	247	1.85	15.3
70	42.0	58.0	624	116	179	245	2.00	15.2
80	55.4	44.6	672	102	176	246	2.29	15.3
90	73.6	26.4	711	97	170	243	3.67	18.9
100	100	0	860	0	185	272	—	—

TABLE XII

55°

% Ac.	p_1 mm.	p_2 mm.	$\frac{p_2}{c_2}$ %	$\frac{p_2}{c_2}$ mol.	$\frac{p_2}{\sqrt{c_2}}$	$\frac{p_2}{\sqrt[3]{c_2}}$	$\frac{p_1}{c_1}$	$\frac{p_1}{\sqrt{c_1}}$	$\frac{p_1}{\sqrt[4]{c_1}}$	$\frac{p_1}{\sqrt[3]{c_1}}$
0	0	117.5	1.175	1.175	11.75	25.3	—	—	—	—
10	157	118	1.31	1.22	12.0	25.7	47.6	86.4	109	105.5
20	283.5	115.5	1.44	1.25	12.0	25.5	39.4	106	177	146.5
30	370.5	107.5	1.53	1.22	11.45	24.15	31.6	108	200	163
40	420	114	1.90	1.38	12.5	26.15	24.5	102	206.5	163
50	472	100	2.00	1.31	11.45	23.6	19.9	97	214	164.5
60	496.5	101.5	2.54	1.49	12.3	24.85	15.6	88	209	157
70	528	93	3.10	1.60	12.2	24.0	12.6	81.5	207.5	152
80	566.5	78.5	3.92	1.76	11.75	22.15	10.2	76	207.5	148.5
90	602	78	7.8	2.95	15.2	26.2	8.18	70	205.5	143.5
100	721	0	0	—	—	—	7.2	72	228	155.5

TABLE XIII

50°

% Ac.	c_1	c_2	p_1 mm.	p_2 mm.	$\frac{p_1}{\sqrt[3]{c_1}}$	$\frac{p_1}{\sqrt[4]{c_1}}$	$\frac{p_2}{c_2}$	$\frac{p_2}{\sqrt{c_2}}$
0	0	100	0	92	—	—	0.920	9.20
10	3.3	96.7	126	95	84.6	93.5	0.982	9.66
20	7.2	92.8	232.5	91.5	120	142	0.986	9.50
30	11.7	88.3	306.5	86.5	135	166	0.975	9.20
40	17.1	82.9	350.5	91.5	136	172	1.10	10.05
50	23.7	76.3	392	80	136	178	1.05	9.16
60	31.8	68.2	414	85	131	174	1.25	10.3
70	42.0	58.0	442.5	75	127	174	1.29	9.85
80	55.4	44.6	477	59	125	175	1.32	8.84
90	73.6	26.4	509	57.5	121	174	2.18	11.2
100	100	0	607	0	131	192	—	—

TABLE XIV

45°

% Ac.	c_1	c_2	p_1 mm.	p_2 mm.	$\frac{p_1}{\sqrt[3]{c_1}}$	$\frac{p_1}{\sqrt[4]{c_1}}$	$\frac{p_2}{c_2}$	$\frac{p_2}{\sqrt{c_2}}$
0	0	100	0	71.5	—	—	0.715	7.15
10	3.3	96.7	101	76	67.7	74.7	0.786	7.15
20	7.2	92.8	192.5	69.5	99.7	118	0.749	7.73
30	11.7	88.3	253	66	111.5	137	0.747	7.22
40	17.1	82.9	293	71	114	144	0.856	7.02
50	23.7	76.3	329.5	61.5	115	149	0.806	7.80
60	31.8	68.2	346.5	67.5	109	146	0.990	7.04
70	42.0	58.0	369	59	106	145	1.04	8.17
80	55.4	44.6	400	47	105	147	1.05	7.75
90	73.6	26.4	423.5	45.5	101	145	1.72	7.04
100	100	0	505	0	109	160	—	8.86

TABLE XV

40°

% Ac.	c_1	c_2	p_1 mm.	p_2 mm.	$\frac{p_1}{\sqrt[3]{c_1}}$	$\frac{p_1}{\sqrt[4]{c_1}}$	$\frac{p_2}{c_2}$	$\frac{p_2}{\sqrt{c_2}}$
0	0	100	0	55	—	—	0.550	5.50
10	3.3	96.7	80	59	53.7	59.3	0.610	6.00
20	7.2	92.8	152.5	56.5	79.0	93.1	0.609	5.87
30	11.7	88.3	206	52	90.7	111	0.589	5.53
40	17.1	82.9	242.5	55.5	94.1	119	0.669	6.16
50	23.7	76.3	271	48	94.4	123	0.629	5.50
60	31.8	68.2	286.5	53.5	90.5	121	0.784	6.48
70	42.0	58.0	305	47	87.9	120	0.810	6.17
80	55.4	44.6	332.5	35.5	87.2	122	0.795	5.32
90	73.6	26.4	350	37.5	83.5	120	1.42	7.30
100	100	0	416	0	89.6	131	—	—

TABLE XVI

35°

% Ac.	c_1	c_2	p_1 mm.	p_2 mm.	$\frac{p_1}{\sqrt[3]{c_1}}$	$\frac{p_1}{\sqrt[4]{c_1}}$	$\frac{p_2}{c_2}$	$\frac{p_2}{\sqrt{c_2}}$
0	0	100	0	42	—	—	0.42	4.2
10	3.3	96.7	62	45	41.5	45.8	0.465	4.58
20	7.2	92.8	122	43	63.1	74.3	0.463	4.46
30	11.7	88.3	166	40	73.0	89.7	0.453	4.26
40	17.1	82.9	196.5	42.5	76.3	96.8	0.513	4.67
50	23.7	76.3	224.5	35.5	78.1	102	0.465	4.06
60	31.8	68.2	233.5	43.5	73.7	98.3	0.638	5.27
70	42.0	58.0	254	36	73.0	99.6	0.620	4.73
80	55.4	44.6	276	25	72.4	101	0.560	3.74
90	73.6	26.4	292	26	69.6	99.6	0.985	5.06
100	100	0	343	0	73.9	108	—	—

TABLE XVII

30°

% Ac.	c_1	c_2	p_1 mm.	p_2 mm.	$\frac{p_1}{\sqrt[3]{c_1}}$	$\frac{p_1}{\sqrt[4]{c_1}}$	$\frac{p_2}{c_2}$	$\frac{p_2}{\sqrt{c_2}}$
0	0	100	0	31.5	—	—	0.315	3.15
10	3.3	96.7	47.5	34.5	31.8	35.2	0.357	3.51
20	7.2	92.8	96	34	49.7	58.6	0.366	3.53
30	11.7	88.3	134	30.5	58.9	72.3	0.345	3.25
40	17.1	82.9	157.5	34	61.2	77.5	0.410	3.73
50	23.7	76.3	182	29	63.4	82.5	0.380	3.32
60	31.8	68.2	189	35	70.7	94.3	0.513	4.24
70	42.0	58.0	205	29.5	59.2	80.8	0.509	3.87
80	55.4	44.6	225	20	58.9	82.4	0.448	2.99
90	73.6	26.4	236.5	21.5	56.5	80.8	0.814	4.18
100	100	0	281	0	60.6	88.9	—	—

TABLE XVIII

25°

% Ac.	c_1	c_2	p_1 mm.	p_2 mm.	$\frac{p_1}{\sqrt[3]{c_1}}$	$\frac{p_1}{\sqrt[4]{c_1}}$	$\frac{p_2}{c_2}$	$\frac{p_2}{\sqrt{c_2}}$
0	0	100	0	23.5	—	—	0.235	2.35
10	3.3	96.7	38	27	25.3	28.0	0.279	2.75
20	7.2	92.8	77	27	39.8	47.0	0.291	2.80
30	11.7	88.3	105	25	46.4	57.0	0.283	2.66
40	17.1	82.9	125.5	24.5	48.7	61.6	0.296	2.69
50	23.7	76.3	146	22	50.8	66.1	0.288	2.52
60	31.8	68.2	152	28	47.9	63.9	0.411	3.39
70	42.0	58.0	164.5	23.5	47.3	64.6	0.405	3.09
80	55.4	44.6	182	16	47.7	66.6	0.370	2.47
90	73.6	26.4	192	17	45.8	65.5	0.663	3.33
100	100	0	229	0	49.3	72.4	—	—

Cornell University

NEW BOOKS

Grundlinien der anorganischen Chemie. *By W. Ostwald. 14 × 22 cm; pp. xix + 795. Leipzig: Wilhelm Engelmann, 1900. Price: linen bound, 16; half leather, 18 marks.* —The first three chapters form the introduction, in which we find a brief but very lucid exposition of our fundamental conceptions in regard to matter, a statement of the facts from which we deduce the laws of the conservation of mass and of energy, together with a discussion of combustion phenomena. Next comes a chapter in which a few words are devoted to each of the elements. This leaves the author free to discuss the elements in almost any order he likes, and permits a corresponding ease in the development of the subject. Successive chapters are then devoted to oxygen, hydrogen, water, hydrogen peroxid, chlorin, oxygen compounds of chlorin, the remaining three halogens, sulfur and its compounds, selenium and tellurium, nitrogen, phosphorus, carbon, silicon, boron, and the gases argon, helium, etc.

The whole treatment is excellent, and the student learns about many things which are ordinarily omitted from an elementary course: rate of diffusion, reversible equilibrium, mass action, catalysis, phase rule, thermochemical relations, dissociation theory, electrolysis and Faraday's law, free energy, theorem of Le Chatelier (not under this name), strength of acids, relation of enantiotropic and monotropic forms, hydrolysis. The discussion of electrolytic dissociation comes in under the first acid, hydrochloric acid, and it is a real pleasure to see the way in which this conception simplifies the whole treatment. It should be noticed that the dissociation theory is deduced from the chemical phenomena. While this was not the way in which the subject actually developed, it has the great pedagogical merit of not requiring from the student facts with which he is not familiar.

Since acids and bases must be treated simultaneously, it might be thought that a study of sodium should come in early in the course. Here we get an admirable instance of the advantage of the preliminary chapter on the elements. The student has been shown sodium just as he has been shown zinc, iron, copper, or mercury. Sodium is acted on by water, forming sodium hydroxid and hydrogen, and the essential properties of sodium hydroxid are taken up before the careful study of sodium. This is perfectly proper, especially when we consider that a base is essentially a compound, containing hydroxyl as ion just as an acid is essentially a substance containing hydrogen as ion.

The second half of the book is devoted to the metals, which are taken up in the following order: potassium, sodium, rubidium etc., calcium, magnesium, strontium etc., aluminum and the rare earths, iron, manganese, chromium, cobalt and nickel, zinc and cadmium, copper, lead, mercury, silver, thallium, bismuth, antimony, arsenic, vanadium etc., tin and the allied metals uranium etc., gold and the platinum metals. The book closes with a chapter on the choice of combining weights and on the periodic law.

There is almost nothing to criticize in the book. The inversion point of sulfur is given as 98°; the false melting-point of 440° is quoted for antimony without comment; and nothing is said about the melting-point of red phosphorus, possibly owing to this portion of the work having been set before the discovery was made. There is one point, however, in which the second edition might show a distinct improvement over the first, namely, by having forward references. In a number of places we find a statement of the general form that "this point will be discussed in detail later". It would add greatly to the value of the book if a reference were given to the page at which that discussion takes place. The reviewer is aware that there are technical difficulties in regard to this; but the matter is so important that it would be well worth while to institute this reform.

There can be no question but that this book marks the beginning of a new pedagogical era. Hitherto physical chemistry has been rather a branch in itself than a manner of looking at the subject. The influence of physical chemistry upon elementary, analytic, inorganic, and organic chemistry has been exerted from the outside. Now, for the first time, we get a reformation from within. Of course, this is not a bolt from a clear sky. Ostwald has been working up to this for years, and at several other universities lectures on elementary chemistry are now given by physical chemists along similar though not identical lines; but these are isolated, almost tentative, efforts, the immediate effect of which is purely local. Most of the people now teaching introductory chemistry have not been trained in physical chemistry, and even if they wish to teach their subject according to the modern scientific views, they are not able to rearrange the subject matter unassisted. This work has now been done by Ostwald and we have the result in printed form, ready to be used by any one.

The reviewer is not so sanguine as to expect that Ostwald's book will at once be adopted throughout the length and breadth of the scientific world. Inertia is as much of a factor in the mind as in the body. There is, however, no longer any justification for teaching chemistry in an unscientific manner, and it is merely a question of time when the right way will be the general way.

The fact that this book will revolutionize the whole teaching of introductory chemistry is a striking illustration of Ostwald's ability as a leader, or rather as an expounder. Ostwald has done much excellent scientific work, few men more or better; but his real strength is as a teacher. It is not an exaggeration to say that the first edition of the *Lehrbuch* created the science of physical chemistry. The facts were all there before Ostwald wrote his book. It is probable that others, like Horstmann, for instance, had seen the subject as a whole before Ostwald. It was Ostwald, however, who made the chemists of the world see the subject as a whole. Van 't Hoff originated the modern theory of solutions, Arrhenius the electrolytic dissociation theory, and Nernst the osmotic theory of the voltaic cell; but it is Ostwald who has developed these theories, who has preached them in and out of season, and who made the scientific world accept them very much against its will. It is to Ostwald that we owe the introduction of a rational point of view into analytical chemistry, the beneficial results of which are now to be seen in the experimental work appearing from Küster's laboratory. It is to Ostwald, lastly, that we owe the reform in the teaching of elementary chemistry, of which the book under review is the first visible sign.

It is not claimed that the arrangement in the book is the best conceivable arrangement. It is by no means certain that there is such a thing as a best arrangement. It has seemed good to Ostwald to treat the non-metals in one group and the metals in another. Another man might prefer a more strictly historical method, and yet other satisfactory arrangements are conceivable. The important point is that this book of Ostwald's gives a thoroughly satisfactory presentation of the subject and that it is incomparably better than any other text-book on introductory chemistry. *Wilder D. Bancroft*

Einführung in die Stöchiometrie, oder die Lehre von der quantitativen Zusammensetzung der Körper und ihren mit dieser Zusammenhängenden Eigenschaften. *By Joachim Biehringer. 15 × 23 cm; pp. xviii + 498. Braunschweig: Friedrich Viewig und Sohn, 1900.* — This is a unique work. It consists of a vast number of problems, the solutions thereof, and text enough to make intelligible the general principles which the problems are designed to illustrate. Nor are these problems mere skeletons. The large majority of them are concrete cases, with sufficient detail to make them seem to the student worth doing. Many of the problems have actually occurred in scientific papers. The following will serve as an instance. "In 1832 Liebig and Wöhler found 68.9 pct. C, 5 pct. H, and 26.1 pct. O in benzoic acid; 36.2 pct. C, 2.2 pct. H, 14.5 pct. O, and 47.1 pct. Ag in the silver salt. What is the molecular weight of benzoic acid?" Other problems have a pseudo-technical look which may prove alluring to the student and certainly can do no harm. "Required to make a sparkling wine from one thousand liters fermented must which contains ten volume-percents of alcohol and 0.5 pct. unfermented sugar. How much sugar must be added to give a sparkling wine under five atmospheres pressure through fermentation at 12°, cellar temperature?" It is probably not the idea of the author that this problem and others of similar nature are to be understood as giving technical instruction; but this problem has the distinct educational advantage that it cannot be solved in a purely routine manner by letting x equal the amount of sugar required, substituting the figures in a formula and obtaining the answer by multiplication and division.

The general arrangement of the book is that developed by Ostwald and is therefore a familiar one, though equally certainly not the best. There are a few minor shortcomings and misprints, but surprisingly few. The final discussion of atomic weights comes at the end of the book, thus necessitating many forward references. It would have been well, in view of the size of the book, to have said a few words more in regard to thermometry, especially about the scale with movable zero. In the problems dealing with gases, the absolute temperature should be used throughout, as it simplifies the calculations. On page 377, "amorphous red phosphorus" is a slip, since the red phosphorus is crystalline. On the same page there is a misprint in regard to the specific weight of orthoclase. One might also cavil at the definition of the boiling-point, as the temperature at which liquid and vapor coexist; but it is not worth while. The book is a good book, and the author has performed in a very creditable manner the task which he has set himself. The task was also one that was worth doing. It is really quite refreshing, once in a while, to come across a book of which one can conscientiously say something good. *Wilder D. Bancroft*

La Tonométrie. *By F. M. Raoult.* (*Scientia No. 8.*) *13 × 19 cm; pp. 116. Paris: Georges Carré et C. Naud. Price: 2 francs.* — This is a little monograph on vapor-pressure measurements. Such books are interesting from two points of view, as showing the present state of the science, and as showing the views of the author in regard to the future development of the subject. The general presentation is a little one-sided, but that is not very surprising when one considers that Raoult worked for years before the general public took any interest in the result. Consequently he looks upon the theoretical developments as little more than a statement of his own work. It seems, however, to have been overlooked that the abnormal results obtained by Ramsay with mercury as solvent have already been explained. In regard to the future developments, everyone will read with interest, though perhaps not with conviction, the chapter on the existence of hydrates in solution. *Wilder D. Bancroft*

Les Phénomènes de Dissolution et leurs Applications. *By V. Thomas.* (*Encyclopedie scientifique des Aide-Mémoire*). *12 × 19 cm; pp. 197. Paris: Gauthier-Villars. Price: paper, 2.5; boards, 3 francs.* — This book is rather a disappointment because many of the data are taken from Étard's work, and it is now pretty clearly understood that Étard's method of making solubility determinations does not lead to accurate results. We also find reproduced many of Étard's theoretical conclusions, and throughout the book there is no reference to the phase rule. There is a chapter on the precipitation of one salt by another, which leaves matters in an unnecessarily tangled state. The great difficulty with the book is that the author is practically acquainted only with French literature on the subject. *Wilder D. Bancroft*

Les Décharges électriques dans les Gaz. *By J. J. Thomson. Ouvrage traduit de l'anglais, avec des notes par Louis Barbillion, et une préface par Ch. Ed. Guillaume. 14 × 23 cm; pp. xiv + 170. Paris: Gauthier-Villars, 1900. Price: 5 francs.* — This is a translation of J. J. Thomson's notable Princeton Lectures on *The Discharge of Electricity through Gases*, which were noticed at length in this Journal 3, 47. The version is introduced by a preface by C. E. Guillaume, who outlines the history of the research in the subject, and comments on the interpretation of the observed phenomena. Thirteen notes have been appended by the translator, for the purpose of giving an account of the work that has been done since the original publication of the book. The lectures deserved translation, and they will doubtless prove very useful in their new form. *J. E. Trevor*

Kurzer Abriss der Electricität. *By L. Graetz. Zweite, verbesserte, Auflage. 16 × 22 cm: pp. viii + 190. Stuttgart: J. Engelhorn, 1900. Price: cloth, 3 marks.* — This is a revised edition of Graetz's little popular treatise on electrical science and its applications, the first edition of which was noticed in this Journal, 3, 240. The new edition, like the old one, gives a simple and carefully arranged account of the more important electrical phenomena, and of the current views in regard to them. The volume is inexpensive, and brings a considerable amount of well-ordered information. *J. E. Trevor*

REVIEWS

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

General

The specific heat of wheat starch as a function of water content and of temperature. *H. Rodewald and A. Kattein. Zeit. phys. Chem.* 33, *540* (*1900*).—Specific heat determinations leading to no general conclusion. *W. D. B.*

The heat of formation of alloys. *J. B. Taylor. Phil. Mag.* [*5*] 50, *37* (*1900*).—"Experiments have been made on the alloys of lead with tin, bismuth, and zinc, and of zinc with tin and mercury. The method employed, which determined the choice of alloys, consisted in dissolving (*a*) the alloy, and (*b*) the corresponding mixture of metals in mercury and measuring the heat of solution in each case." With lead and zinc, lead and bismuth, tin and zinc, the difference between the two heats of solution was very marked. The author does not correlate these phenomena with any others, thus omitting the really important part of the work. *W. D. B.*

Poly-Component Systems

On the solubility of hydrated mix-crystals, III. *W. Stortenbeker. Zeit. phys. Chem.* 24, *108* (*1900*).—Cadmium and ferrous sulfates form two series of mix-crystals, one with seven of water, the other with two and two-thirds. The author has determined an isotherm. At 18° the order of crystallization with manganese and copper sulfates is mix-crystals with five, with seven, and again with five of water. It is now shown that above 23° there is a continuous series of crystals with five of water, those with seven being instable. The paper closes with a discussion of the change in concentration of mix-crystals on standing in contact with the solution. *W. D. B.*

On the mechanism of gelation in irreversible colloidal systems. *W. B. Hardy. Proc. Roy. Soc.* 66, *95*; *Zeit. phys. Chem.* 33, *326* (*1900*).—Published (4, 256).

A preliminary investigation of the conditions which determine the stability of irreversible hydrosols. *W. B. Hardy. Proc. Roy. Soc.* 66, *110*; *Zeit. phys. Chem.* 33, *385* (*1900*).—Published (4, 235).

On gelatinization and moistening phenomena. *H. Rodewald. Zeit. phys. Chem.* 33, *593* (*1900*).—The author assumes that the heat effect due to moistening starch will vary suddenly so soon as the condensed water-layer exceeds one molecule in thickness. Various corrections are then introduced and the molecular weight of starch is estimated not to exceed 68000 in case the starch molecule is spherical and not to exceed 45000 in case the molecule is cubical.

W. D. B.

On natural and artificial starch grains. *H. Rodewald and A. Kattein. Zeit. phys. Chem.* 35, *579* (*1900*). — The authors bring wheat starch into solution by heating with iodin to 130°, free the solution from iodin, and effect a precipitation of starch grains. They have made a quantitative study of this artificial starch, and of five natural starches. The final conclusion is that the artificial starch possesses all the characteristics of natural starch, though not identical with any one of the natural starches. Osmotic pressure measurements point to a molecular weight of about 37000; but no significance is really to be attributed to this value, though the authors apparently fail to realize this.

W. D. B.

On the behavior of a mixture of benzene vapor and hydrogen in the presence of platinum or palladium black. *G. Lunge and J. Akunoff. Zeit. anorg. Chem.* 24, *191* (*1900*). — Palladium black causes hydrogen and benzene to unite, forming tetrahydrobenzene; platinum black causes the formation of hexahydrobenzene. In order to keep the platinum effective, it must occasionally be treated with hydrogen containing no benzene. The statement of Harbeck and Lunge that benzene and hydrogen do not react in presence of platinum black probably refers to experiments made with an accidentally spoiled platinum black.

W. D. B.

Oxidation by means of free oxygen. *W. Ostwald. Zeit. phys. Chem.* 24, *248* (*1900*). — This is a curious mixture of clearness and haziness. The problem is to account for the formation of ozone when oxygen acts on phosphorus, ozone having a higher potential than oxygen. It is pointed out very properly that such a rise of potential can occur only when necessarily accompanied by a fall of potential elsewhere, and it is also shown that, for this to take place, the two reactions must be connected in some stoichiometric relation. So far this is very good, though outlined by Gibbs over twenty years ago. The next step, which is very hazy indeed, is that this can take place only in case an intermediate compound is formed, which then dissociates. It is perfectly true that the desired stoichiometric relations follow necessarily in case such an intermediate compound is formed; but it has not been proved that such stoichiometric relations can exist only in case such a compound occurs. In fact, the hypothesis of van 't Hoff, to which no reference is made, is evidence to the contrary.

W. D. B.

Velocities

On the rate of formation of the olefins from aliphatic iodids. *S. Brussoff. Zeit. phys. Chem.* 24, *129* (*1900*). — By the action of alcoholic potash on aliphatic halids, there may be formed an olefin or an ether, or both simultaneously. In Wildermann's experiments only the total change was studied, while the author has determined the amount of olefin in each case, and has based his calculations thereon. The reaction velocity increases at first and then decreases very nearly as required for a monomolecular reaction. The first peculiarity is explained by the author as due to temperature changes, the second is apparently not looked upon by him as surprising. [Since an excess of potash was always taken, the percentage excess would increase as the reaction progressed and the reaction would in time become practically monomolecular.] The replacement of caustic potash by caustic soda or of ethyl alcohol by methyl alcohol had but slight effect. *W. D. B.*

On the reaction velocity constants in the formation of simple ethers. *W. Sagrebin. Zeit. phys. Chem.* 24, *149* (*1900*). — The reaction studied was that of an alcohol in excess on the corresponding ester of benzene sulfonic acid. A very good constant was obtained for a monomolecular reaction without taking into account any catalytic action due to the benzene sulfonic acid. The constants obtained are not strictly comparable, owing to the solvent changing from one case to the next. *W. D. B.*

The effect of chemically indifferent solvents on reaction velocities. *N. Menschutkin. Zeit. phys. Chem.* 24, *157* (*1900*). — Instances are given in which the relative rate of two reactions is reversed by changing the solvent. In determining questions of structure by means of reaction velocity experiments, it is therefore essential to work with those solvents for which the effect of that particular structure is most marked. *W. D. B.*

The effect of the medium on reaction velocity. *G. Buchböck. Zeit. phys. Chem.* 24, *229* (*1900*). — The author has studied the effect of salts and acids on the rate of decomposition of carbonyl sulfid. With isotonic solutions of inorganic compounds, the product of reaction velocity into internal friction is a constant; this is not true for the substituted acetic acids. Here, however, the volume occupied by the solute is larger and it was found that in all cases the above-mentioned product is a linear function of the total amount of water. [This is a striking instance of the way in which the recognition of the changing concentration of the water simplifies matters.] *W. D. B.*

Electromotive Forces

The thermodynamics of normal cells. *E. Cohen. Zeit. phys. Chem.* 24, *62* (*1900*). — The author points out that it is not permissible to consider the reaction in the Clark cell as

$$Zn + Hg_2SO_4 + Aq \rightleftarrows 2Hg + ZnSO_4 7H_2O.$$

The real reaction is

$$Zn + \frac{7}{A-7} ZnSO_4 AH_2O + Hg_2SO_4 \rightleftarrows 2Hg + \frac{A}{A-7} ZnSO_4 7H_2O,$$

where A is the ratio of reacting weights of water to reacting weights of zinc sulfate in the saturated solution at the temperature under consideration. From the Helmholtz equation, the heat of reaction comes out as 814.9 K; from the thermochemical data, we get 777.8 K according to the first equation and 811.3 according to the second. *W. D. B.*

Theory of the third form of inversion cell. *E. Cohen. Zeit. phys. Chem.* 24, *178* (*1900*). — Under this head come a pair of opposed Clark cells when the solid salt is the stable form in one cell and the metastable form in the other. The author has determined the change of solubility with the temperature of the two hydrated zinc sulfates in the neighborhood of 33° and has also determined the heat of reaction at the same temperature. From these data he calculates the temperature coefficient of the cell as —0.52 millivolt, while the experimental value is —0.50 millivolt. *W. D. B.*

The transference number of sulfuric acid solutions from measurements on the lead accumulator. *A. Kendrick. Zeit. Elektrochemie,* 7, *52* (*1900*). — The author has used the Helmholtz method to determine the transference numbers of sulfuric acid solutions of different concentrations, using lead electrodes, lead peroxid electrodes, and hydrogen electrodes. The values of *n* for the cation from the lead and hydrogen electrodes run some three hundredths lower than those from the lead peroxid and hydrogen electrodes. In consequence, the real transference numbers for sulfuric acid solutions are still doubtful. *W. D. B.*

The supposed identity of red and yellow mercuric oxid. *E. Cohen. Zeit. phys. Chem.* 24, *69* (*1900*). — Previous measurements by Mark had shown that the difference in free energy between red and yellow mercuric oxid was less than 1-2 millivolts, and it was therefore assumed that the two were identical. It has now been shown that the two are distinct forms, the difference of free energy being nearly 0.7 millivolt at 25°. *W. D. B.*

Potentials of copper electrodes in solutions containing analytically important copper precipitates. *C. Immerwahr. Zeit. anorg. Chem.* 24, *269* (*1900*). — Measurements against the normal electrode of copper in solutions saturated with respect to different copper salts. *W. D. B.*

Studies on oxidation potentials. *F. Crotogino. Zeit. anorg. Chem.* 24, *225* (*1900*). — Under proper conditions it should be possible to oxidize a mixture of iodids and bromids with permanganate solution so that iodin only should be set free. This was the case, but it proved impossible to remove the iodin completely. On titrating with permanganate, using the electrometer as indicator, it was found possible to determine the amount of iodid present, but not the amounts of bromin or chlorin. Attempts to study the potential of oxidizing agents in the presence of varying amounts of acid proved unsuccessful, owing to the inconstant results. Constant results were obtained with an iodin solution so long as the solution was saturated with respect to iodin; otherwise not. Measurements of the oxygen electrode against an air electrode gave values much higher than those required by the theory. *W. D. B.*

Correction to my paper on the theory of the lead accumulator. *F. Dolezalek. Zeit. Elektrochemie,* 6, *557* (*1900*). — In the previous paper (4, 153) the author assumed that the decrease in the vapor-pressure of the dissolved lead sulfate can be neglected in comparison with the corresponding change in the sulfuric acid. Dropping this assumption, which is untenable for a dilute acid, the lead sulfate is found to be five percent hydrolyzed instead of fifteen percent, while the calculation of the dissociation of water drops out. *W. D. B.*

On the temperature coefficient of the lead accumulator. *F. Dolezalek. Zeit. Elektrochemie*, 6, *517* (*1900*). — The temperature coefficient of the accumulator is negative for very dilute acid, but increases with the concentration, passing through zero for 0.7 *n* acid, reaching a maximum with double normal acid and then decreasing with increasing concentration. There is a difference of 0.6 V if two cells with very dilute acid are kept, one at 10° and the other at 100°.

W. D. B.

On gas polarization in the lead accumulator. *W. Nernst and F. Dolezalek. Zeit. Elektrochemie*, 6, *549* (*1900*). — A steady current of gas is given off when sulfuric acid is electrolyzed between platinum electrodes under a potential difference of 1.7–1.9 volts, while a voltage of 2.5 volts is necessary when lead electrodes are used. The authors account for this by the assumption that the decomposition voltage consists of a value for the electrolyte plus terms for the electrodes. They show that lead sulphate is more readily reduced at a lead than at a platinum cathode, but that the reduction can be made to take place at the platinum cathode by increasing the current density. *W. D. B.*

On gas polarization in the lead accumulator. *Strasser and Gahl. Zeit. Elektrochemie*, 7, *11* (*1900*). — The authors show that the presence even of considerable quantities of antimony does not affect the potential of the accumulator, while hydrogen is precipitated more readily on an alloy of lead and antimony than on pure lead. *W. D. B.*

The decomposition voltage for chlorin. *E. Müller. Zeit. Elektrochemie*, 6, *573*, *581* (*1900*). — Normal hydrochloric acid shows a decomposition point at about 1.3 V, and it has always been assumed that this represented the evolution of gaseous hydrogen and chlorin. Müller suggests that this value may be due to the oxidizing action of chlorin, pointing out that the acid and alkaline (not neutral) cells with hydrogen and hypochlorite at the electrodes give approximately 1.3 V. There should therefore be another point at which gaseous chlorin is evolved and the author gives experiments to show that this occurs when the anode potential is 2.2 V, the calomel electrode being taken as 0.56 V.

W. D. B.

On a method for determining decomposition voltages with the capillary electrometer. *E. Müller. Zeit. Elektrochemie*, 6, *543* (*1900.*) — The electrodes are placed in shunt with a wire between the ends of which there is a known, but variable potential difference, and the electromotive force of polarization is then determined. If no current is passing, this value will equal the potential difference between the ends of the wire, otherwise not. *W. D. B.*

On a practical form of normal element and normal electrode. *E. Bose. Zeit. Elektrochemie*, 6, *457* (*1900*). — The author uses a modified Hempel desiccator with mercury at the bottom and amalgam where the sulfuric acid would naturally be. The advantages are large electrode surface and relatively small internal resistance. *W. D. B.*

On a bridge arrangement for polarization measurements devised by H. Luggin. *F. Haber. Zeit. Elektrochemie*, 7, *13* (*1900*). — A piece of apparatus for tapping off a definite potential difference. *W. D. B.*

Electrolysis and Electrolytic Dissociation

On the electrolytic synthesis of organic substances, I. *A. Dony-Hénault. Zeit. Electrochemie,* **6**, *533* (*1900*). — The decomposition-point of hydrochloric acid is lowered by the presence of phenol and it should therefore be possible to obtain a quantitative yield of chlorin substitution products of phenols. The precipitation of these compounds on the electrode interfered with the process and attention was next turned to the electrolytic oxidation of alcohol. The presence of acetaldehyde reduces the decompositson potential of sulfuric acid but slightly, while alcohol reduces it a good deal. It should therefore be possible to oxidize alcohol electrolytically to acetaldehyde with theoretical efficiency, and this was actually accomplished by keeping the potential difference between the anode and a hydrogen electrode 0.7–1.0 volt. No data are given as to the composition of the solution or the quantity taken, but the hundred percent efficiency refers to experiments in which 32–180 milligrams of acetaldehyde were prepared.

It must also be possible to oxidize alcohol to acetaldehyde with chemical reagents, provided we take an oxidizing agent having the proper potential against the hydrogen electrode. Lead peroxid or cuprous oxid in alkaline solution oxidizes alcohol to acetaldehyde; acid and neutral potassium ferrocyanid have no effect; while alkaline ferrocyanid carries the oxidation too far.

W. D. B.

On the electrolytic synthesis of organic substances, II. *O. Dony-Hénault. Zeit. Elektrochemie,* 7, *57* (*1900*). — It is shown that the addition of alcohol to a solution of potassium iodid and sodium carbonate does not affect the decomposition voltage, whence the conclusion is drawn that the formation of iodoform is due to a secondary reaction. It is then shown that the primary reaction is the formation of hypoiodite, and that this then reacts with the alcohol.

W. D. B.

Electrolytic preparation of indulin dye-stuffs. *E. C. Szarvasy. Zeit. Elektrochemie,* **6**, *403* (*1900*). — When fused anilin hydrochlorid is electrolyzed between carbon electrodes, a blue dye-stuff is formed at the anode. Azophenin was also prepared in considerable quantities. It appears that there is oxidation at the anode to azo compounds and that these react with anilin hydrochlorid, forming azophenin and indulin dye-stuffs. *W. D. B.*

On the electrolytic preparation of indulin dye-stuffs. *W. Löb. Zeit. Elektrochemie,* **6**, *441* (*1900*). — The author dissolves nitro compounds in a solution of anilin in concentrated hydrochloric acid and then reduces electrolytically at ordinary temperature. When the reduction has reached the azo stage, the products react with the anilin hydrochlorid, forming what are probably indulin dye-stuffs. Azophenin was not observed. *W. D. B.*

On the electrolytic reduction of difficultly reducible substances in sulfuric acid solutions. *J. Tafel. Zeit. phys. Chem.* 24, *187* (*1900*). — The experiments were made with caffein and it was found that lead and mercury cathodes are the most effective. These are both substances which call for a distinct excess voltage before hydrogen can be precipitated. It is essential that the lead should be very pure and that the surface should be rough, preferably covered with spongy lead. Increasing the temperature increases the yield somewhat. *W. D. B.*

On the electrolytic reduction of paranitro-anilin. *H. Sonneborn. Zeit. Elektrochemie*, 6, *509* (*1900*). — When paranitro-acetanilid is reduced electrolytically in aqueous alcoholic solution, the chief product is acetyl-*p*-phenylendiamin. If the solution be kept continually neutral, there is also formation of diacetyl-*p*-diamido-azoxybenzene. *W. D. B.*

Investigations on the electrolytic oxidation of the aliphatic alcohols. *K. Elbs and O. Brunner. Zeit. Elektrochemie*, 6, *604* (*1900*). — With smooth platinum anode and an aqueous solution containing 160 g methyl alcohol and 49–98 g sulfuric acid per liter, an eighty percent yield of formaldehyde is obtained when working at 30° with an anode density of 0.0375 amp/cm^2. Increasing the amount of alcohol causes formation of methylal; platinizing the anode reduces the yield one-half. With ethyl alcohol, propyl alcohol and isoamyl alcohol, the corresponding acid is the main product. With isopropyl alcohol a seventy percent yield of acetone was obtained. These efficiencies are, of course, electrical efficiencies. *W. D. B.*

The electrolytic preparation of hypochlorites. *A. Sieverts. Zeit. Elektrochemie*, 6, *365, 374* (*1900*). — Experiments with a five percent calcium chlorid solution, eighteen and three percent potassium chlorid solutions in a continuous flow apparatus showed that the percentage yield of hypochlorite increased with increasing anode density. The author was unable to duplicate Schoop's experiments.

Electrolyzed solutions of potassium and sodium chlorids do not bleach as rapidly as a corresponding solution of calcium chlorid because the latter contains free hypochlorous acid. When magnesium chlorid solutions are electrolyzed, there is a marked evolution of chlorin owing to the extreme insolubility of magnesium hydroxid. *W. D. B.*

The electrolysis of sodium chlorid. *R. Lorenz and H. Wehrlin. Zeit. Elektrochemie*, 6, *389, 408, 419, 437, 445, 461* (*1900*). — The authors have worked with finite currents as did Foerster and have also studied the potential differences at the two electrodes as did Wohlwill. Their conclusion is that chlorin is always set free at the anode, forming hypochlorite. The direct formation of chlorate begins when the polarization at the anode is markedly greater than the counter electromotive force. This would imply formation of chlorate by simultaneous discharge of chlorin and hydroxyl as ions. *W. D. B.*

The chlorate formation: reply to Professor Foerster. *H. Wohlwill. Zeit. Elektrochemie*, 6, *412* (*1900*). — In this reply to Foerster (4, 155) the author makes the points that we have no right to assume that hydroxyl as ion may not be discharged in neutral solutions nor that hypochlorite as ion is discharged more easily than chlorin as ion. *W. D. B.*

Anodic evolution of oxygen during the electrolysis of alkali chlorid solutions. *F. Foerster and H. Sonneborn. Zeit. Elektrochemie*, 6, *597* (*1900*). — No alkali was allowed to diffuse from the cathode to the anode chamber. With triple-normal chlorid solution, the yield of oxygen is about two-tenths of one percent, increasing to five percent with three-tenths normal solution. This tends to show that the primary action is the evolution of chlorin and the consequent formation of hypochlorite, which then is or is not stable, depending on the conditions. *W. D. B.*

Note on the electrolysis of fused salts. *F. Quincke. Zeit. anorg. Chem.* 24, *220* (*1900*). — When fused salts are electrolyzed without any special precautions, the amount of metal precipitated is not equal to that required by Faraday's law. The author attributes this to the fact that precipitation occurs only when internal resistance exceeds a certain minimum value. This would seem to be a case of putting the cart before the horse. *W. D. B.*

The electrolysis of fused salts. *R. Lorenz. Zeit. anorg. Chem.* 24, *222* (*1900*). — Reply to Quincke (preceding review). *W. D. B.*

Electrolytic preparation of zinc, using an insoluble anode. *J. Rontchewsky. Zeit. Elektrochemie,* 7, *21*, *29* (*1900*). — The object of this investigation was to precipitate zinc electrolytically and, at the same time, make a marketable substance in the anode chamber. Lead was therefore used as anode and a small amount of sodium chlorate added to the solution of zinc sulfate and sulfuric acid. Under these circumstances, metallic zinc free from lead is precipitated at the cathode in a coherent mass, while lead peroxid is formed at the anode and falls to the bottom of the cell. The most favorable results with regard to lead peroxid were obtained with an anode density of 0.01 amp/cm^2.

Another set of experiments was carried through, in which a diaphragm was used, the anode solution containing sodium chlorate, and sodium chromate or chromic acid, while the cathode solution contained zinc sulfate and sulfuric acid. The anode product, lead chromate, can be used as a paint. The results were very satisfactory, there being no trace of chromic or chloric acid in the cathode solution even after twelve hours electrolysis, while a very good quality of lead chromate was obtained. *W. D. B.*

A chromium cell for the rectification of alternating currents. *J. L. R. Morgan and W. A. Duff. Jour. Am. Chem. Soc.* 22, *331* (*1900*). — A cell consisting of a chromium anode and platinum cathode in sulfuric acid will neutralize a potential difference of 75 V, provided the potential difference is impressed gradually. If the potential difference exceeds this value or is impressed too rapidly, the cell breaks down and the current passes freely. On making the chromium the cathode for a few minutes, in a direct current circuit or by reducing the potential difference to some not very sharply defined value, a reversal takes place and the chromium becomes passive. *W. D. B.*

On electric furnaces with special reference to the preparation of calcium carbid. *B. Carlson. Zeit. Elektrochemie,* 6, *403* (*1900*). — The author discusses the relative advantages of the continuous and discontinuous processes of making calcium carbid, deciding in favor of the latter. The chief merits of the discontinuous process are lower initial temperature and richer product, owing to the continued formation of carbid while the mass is cooling. *W. D. B.*

On continuous and discontinuous carbid furnaces. *O. Fröhlich. Zeit.*

Elektrochemie, 7, *1* (*1900*). — A reply to Carlson (preceding review). The author claims that the temperature at which the carbid is drawn off is as low in the best continuous furnaces as in the discontinuous furnaces and that the initial temperature is lower. It is further stated that reports as to efficiencies are for the most part untrustworthy owing to the large errors (as much as twenty percent) in the electrical measuring instruments. *W. D. B.*

On the arrangement for illustrating the migration and precipitation of the ions. *E. Müller. Zeit. Elektrochemie*, 6, *589* (*1900*). — An ingenious mechanical device for illustrating Hittorf's law of the migration of the ions. It should prove serviceable in class-room work. *W. D. B.*

The ionization of dilute solutions at the freezing-point. *W. C. D. Whetham. Phil. Trans.* 194 A, *321* ; *Zeit. phys. Chem.* 33, *344* (*1900*). — The author has made conductivity measurements at zero in a platinum vessel, starting with a dilute solution and increasing the concentration. The resulting dissociation curves are not identical with those obtained at 18°. The peculiarities, which had been found in the glass vessels, for the conductivity of very dilute solutions of acids and bases recur when platinum is substituted throughout for glass. The author believes that these peculiarities cannot be due to impurities in the water, because it was found possible to make a satisfactory correction for them, while this could be done in the case of the analogous curve for potassium permanganate. It was noticed that with dilute solutions of sulfuric acid the initial resistance is not the same as the final resistance, there being a continuous increase lasting half an hour. The author is inclined to connect the behavior of dilute solutions of acids and alkalies with the fact that these substances have each an ion in common with the solvent. *W. D. B.*

The coagulative power of electrolytes. *W. C. D. Whetham. Phil. Mag.* [*5*] 48, *474* (*1899*). — If we assume "that a certain minimum electrical charge has to be brought within reach of a colloidal group in order to produce the aggregation of colloidal particles which constitutes coagulation, we shall get equal charges by the conjunction of $2n$ triads, $3n$ diads, or $6n$ monads, where n is any whole number." It is then shown that the ratio of the concentrations of equicoagulative solutions can be expressed by the equation $c_1 : c_2 : c_3 = 1 : 1/x : 1/x^2$, where c_1, c_2, and c_3 represent the concentrations of monads, diads, and triads, respectively, and $x = B^{1/6n}$, where B is an arbitrary constant. *W. D. B.*

The color of picric acid and its solution. *W. Marckwald. Ber. chem. Ges. Berlin*, 33, *1128* (*1900*). — Picric acid crystallized from concentrated hydrochloric acid is deposited as colorless crystals. On the addition of water to the acid or to the filtrate, the yellow color is restored. Perfectly dry picric acid loses its color almost completely. These phenomena may be explained by assuming that the pure dry acid is nearly colorless, but that the ion $C_6H_2(NO_3)_3O$ is yellow. By the addition of a strong acid to the solution, the dissociation is forced back and the concentration of the anions is decreased. As a lecture experiment this may be shown by dissolving picric acid in a non-dissociating medium such as ligroin. The solution is colorless. On shaking with water, the ligroin solution is colored yellow. *C. G. L. W.*

Dielectricity and Optics

On the electromagnetic rotation of solutions of salts and acids. *J. Forchheimer. Zeit. phys. Chem.* 24, *20* (*1900*). — The molecular rotation in aqueous solution is independent of the concentration with ammonium, sodium, magnesium, and hydrogen sulfates, and with cadmium bromid and chlorid; it increases with increasing dilution with lithium sulfate and chlorid and with hydrochloric acid. *W. D. B.*

On tautomeric changes in solutions. *J. W. Brühl. Zeit. phys. Chem.* 24, *31* (*1900*). — A study of the optical properties of solutions of tautomeric substances. The scientific value of the paper would have been increased, had the author recognized more clearly the fact that reactions in homogeneous systems do not usually run to an end. *W. D. B.*

The indices of refraction of ethyl ether near the critical point. *B. Galitzin and J. Wilip. Bull. Acad. Sci. St. Petersburg*, (*5*) 11, *117* (*1899*). — The authors have measured the indices of refraction of ether in the neighborhood of the critical point by the lens and by the prism method. When the contents of the tube are kept well stirred, the critical temperature can be determined with a very satisfactory degree of accuracy by observing the temperature at which the indices of refraction for liquid and vapor become identical. When there is not effective stirring, there may be a very marked difference of density between the upper and lower portions of the tube even at temperatures five degrees above that of the critical point. A careful investigation showed that this discrepancy could not be due to temperature differences nor to the effect of gravity, except in part. The authors look upon it as a case of superheating, the liquid phase persisting above the critical temperature. Unfortunately, they do not discuss the theoretical significance of this point, though it would seem to follow from this hypothesis that the critical point was really an intersection point. *W. D. B.*

On the change with the temperature of the specific rotation of sugar. *O. Schönrock. Zeit. phys. Chem.* 24, *87* (*1900*). — For nearly normal sugar solutions the author finds the relation

$$[\alpha]^D_t = [\alpha]^D_{20} \left\{ 1 - 0.000217\,(t - 20) \right\}.$$

W. D. B.

On the relation between the constitution and the fluorescence of some substances. *J. T. Hewitt. Zeit. phys. Chem.* 24, *1* (*1900*). — The author assumes that the change of wave-length with fluorescent substances is due to a change of constitution, in other words that such compounds are tautomeric. An examination shows that this is very generally, though by no means universally, true. *W. D. B.*

On the phosphorescence of phosphorus pentoxid. *H. Ebert and B. Hoffmann. Zeit. phys. Chem.* 24, *80* (*1900*). — Pure phosphorus pentoxid shows a marked green phosphorescence. *W. D. B.*

On the influence of small admixtures on the spectrum of a gas. *P. Lewis. Wied. Ann.* 69, *398* (*1899*). — The spectrum of pure hydrogen gas is examined and compared with the spectrum when a small trace of mercury vapor, oxygen or water vapor is added. The oxygen spectrum is also examined pure, and when mixed with traces of hydrogen, or mercury vapor. The clearness of the effect produced by the impurity is studied in its relation to the pressure of the gas. *H. T. B.*

On the refractive power of some hydrocarbons with several benzene nuclei. *A. Chilesotti. Gazz. chim. Ital.* 30, *I*, *149* (*1900*). — The molecular refraction of naphthalene, anthracene, phenanthrene, and pyrene can be calculated provided we allow 1.46 for each 'central valence'. *W. D. B.*

The specific rotation of some complex salts of tartaric and malic acids. *Arthur Rosenheim and Hermann Itzig. Ber. chem. Ges. Berlin*, 33, *707* (*1900*). — In continuation of the investigation of the stable compounds of molybdenum and tungsten with oxalic acid, tartrates and malates of these metals have been examined. Solutions containing known quantities of the acids with the alkaline salts of the tungstates and molybdates were examined polarimetrically.

In tartaric acid solution, the meta-tungstates do not increase optical activity. Para-tungstates increase the rotation and a maximum is reached when the molecular relation of the tungstate tartaric acid is as 1–5, i. e., when two alkaline ions are present with one tartaric acid ion.

The maximum with the para-molybdates is found in the same relation. A number of the complex molybdo- and tungsto-tartrates were prepared and analyzed. The corresponding malates will be examined by Walden.

C. G. L. W.

REACTION VELOCITY AND EQUILIBRIUM

BY WILDER D. BANCROFT

In the last dozen years a number of reaction velocities have been studied where the order of the reaction was lower than that to be deduced from the formula describing the reaction. The hypothesis, which has been advanced to explain this phenomenon, is that the reactions in question take place in one or more stages, and that if we consider the reaction taking place in some one of these stages only, we shall be able to deduce a formula which will correspond with that found experimentally. It so happens that none of these abnormal reactions have been reversible, and it is therefore not surprising to find irreversibility postulated as a necessary pre-requisite to an abnormal reaction. Ostwald has discussed the matter from this point of view.[1]

"We must now ask how these hypotheses are to be reconciled with the relations, previously discussed, between the formula for reaction velocity and that for chemical equilibrium. The answer is that these relations are not applicable in these cases, and that therefore there is no difficulty on this point. This must be so because the assumption underlying the explanation was that the products of the primary reaction were immediately further changed by a secondary reaction. Under these circumstances the essential condition of chemical equilibrium is lacking, that the reaction products react to form the original substances; consequently the laws of equilibrium are not applicable to these cases.

"In this last consideration we can probably find a criterion for the correctness of these hypotheses, because differences between the order of reaction and the number of molecules taking

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[1] Lehrbuch, 2, II, 243.

part should be possible only when the process is irreversible; the number of molecules and the order of reaction should agree in processes where the original substances can be formed from the reaction products. Too few reactions have been studied as yet from this point of view to enable one to state finally whether this requirement is satisfied experimentally or not."

This is entirely clear. Abnormal reaction velocities cannot occur when the reactions are reversible. It will be desirable to examine this a little more closely. In order to deal with concrete substances, let us take the equilibrium between ammonium carbamate and its dissociation products, all in the gaseous phase and we will first make the assumption that the reaction takes place in one stage according to the equation

$$2NH_3 + CO_2 \rightleftarrows NH_4CO_2NH_2,$$

and then the assumption that the reaction takes place in two stages according to the equations

$$NH_3 + CO_2 \rightleftarrows NH_2CO_2H$$
$$NH_3 + NH_2CO_2H \rightleftarrows NH_4CO_2NH_2,$$

the final concentration of NH_2CO_2H to be practically negligible. Under the first assumption, we will let 2A be the initial concentration of NH_3, B of CO_2, and we will let x be the concentration of $NH_4CO_2NH_2$ at any moment. We may then write

$$\frac{dx}{dt} = k_1(A - x)^2(B - x) - k_2x.$$

For equilibrium we shall have

$$Kx = (A - x)^2(B - x).$$

Under the second assumption we will let $y =$ the concentration of NH_2CO_2H at any moment, the signification of A, B, and x remaining as before. We may then write

$$\frac{dy}{dt} = k_3(A - x - y/2)(B - x - y) - k_4y,$$
$$\frac{dx}{dt} = k_5(A - x - y/2)y - k_6x.$$

For equilibrium $dx/dt = 0$ and $dy/dt = 0$, therefore

$$K_1 y = (A - x - y/2)(B - x - y)$$
$$K_2 x = (A - x - y/2) y.$$

Multiplying these last two expressions, we have

$$K_3 x = (A - x - y/2)^2 \cdot (B - x - y).$$

Since y is by definition practically zero, this is the theoretical equation for equilibrium. We thus see that if the NH_2CO_2H were used up as fast as formed we should have a reaction of the second order if we studied reaction velocity, though the chemical equation would call for a reaction of the third order. From this, it is clear that abnormal reaction velocities may and probably do occur even in the case of reversible reactions.[1] That none have yet been found experimentally is not surprising when one recalls how few reversible reactions have been studied.

It is now possible to drop one limitation. In the discussion, it has been assumed explicitly that the final amount of NH_2CO_2H is zero. Even supposing this were not the case, the concentration of the ammonia is $(2A - 2x - y)$, of the carbonic acid $(B - x - y)$, and of the ammonium carbamate x, so that the last equation is the theoretical equation for equilibrium between ammonium carbamate, ammonia, and carbonic acid. If we drop the further explicit assumption that the NH_2CO_2H remains constantly at its equilibrium concentration, we shall no longer get a perfect constant for a reaction of the second order; but, during the first stages, at any rate, the reaction may be more nearly of the second order than anything else.

The lack of necessary connection between the order of a reaction and the final equilibrium offers a strong argument against the common pedagogical practice of treating reaction velocities first and deducing equilibrium relations from them. The equilibrium phenomena are the fundamental ones and are based solely on analytical data. If we know the equation representing the reaction, we can predict the form of the equilibrium

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[1] Cf. Nernst. Theor. Chem. 3rd. Ed., 523.

equation. We cannot predict the form of the reaction velocity equation from a knowledge of the initial and final concentrations; we cannot predict it from anything. If we know the order of the reaction and the analytical data, we can then say that the reaction takes place in one or more stages — even then, only in case we have not overlooked some catalytic action. The only sound method is to teach the equilibrium phenomena as based on the stoichiometric relations, and then to consider reaction velocities as far as possible with relation to the expressions for equilibrium.

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DIFFERENCES OF POTENTIAL BETWEEN METALS AND NON-AQUEOUS SOLUTIONS OF THEIR SALTS, II

BY LOUIS KAHLENBERG

According to Nernst, the E. M. F. of a galvanic chain of the type

$$\mathrm{Ag}\,|\,\mathrm{AgNO_3(concentrated)}\,|\,\mathrm{AgNO_3(dilute)}\,|\,\mathrm{Ag}$$

may be calculated by means of the formula[1]

$$\pi = \frac{RT}{n_e e_0} \log \frac{C_1}{C_2},$$

when the minor difference of potential at the junction of the two liquids is not taken into account. In this formula π is the E. M. F. of the combination, R the gas constant, T the absolute temperature, n_e the valence of the metal, e_0 the constant of Faraday's law, and C_1 and C_2 the concentrations of the cations, corresponding to the metal of the electrodes, in the concentrated and dilute solutions respectively. Thus far a fair degree of agreement between observed and calculated values of the E. M. F. has been obtained in the case of a number of chains of this character in which water is used as a solvent.

This formula was developed by Nernst on the basis of the assumption that a metal has a definite electrolytic solution tension toward a solvent, and that the osmotic pressure of the ions — of the same nature as the electrode — in the solution opposes this solution tension. In a previous article[2] on this subject, it was shown that if such electrolytic solution tension be assumed to exist, it must further be held that it changes greatly with the nature of the solvent, and indeed with the presence of other dissolved substances contained in the solvent.

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[1] Compare, for instance, LeBlanc, *Lehrbuch der Elektrochemie.*

[2] Kahlenberg. Jour. Phys. Chem. 3, 379 (1899).

The validity of this formula in cases where non-aqueous solutions are employed in galvanic chains of the type under consideration, has, to my knowledge, not been tested. Such a test seemed desirable because it would determine the applicability of Nernst's theory to the case of non-aqueous solutions.

As is evident from the formula, by using but one solvent in the chain, the troublesome quantity, the solution tension, has been eliminated, it being the same on both sides of the galvanic combination. Now C_1 and C_2 are clearly equal to the concentration of the salt in the respective solutions multiplied by the corresponding degree of dissociation. It is necessary, then, to know the latter in each case. How difficult it is to ascertain the degree of dissociation of salts in non-aqueous solutions was shown in my previous article.[1] Indeed it was pointed out clearly that, according to molecular weight determinations, salts are frequently undissociated and yet are good conductors of electricity, a fact which is not compatible with the theory of electrolytic dissociation.

Assuming the theory of electrolytic dissociation, the degree of dissociation of a salt may be calculated according to the formula $\frac{\mu_v}{\mu_\infty}$, where μ_v is the molecular conductivity of a solution containing 1 g-mol of the salt in V liters, and μ_∞ the molecular conductivity at infinite dilution.

If, in the above chain, S_1 and S_2 represent the concentrations of the salt in the concentrated and dilute solutions respectively, then the formula for the E. M. F. becomes

$$\pi = \frac{RT}{n_e e_0} \log \frac{S_1 \frac{\mu_{v_1}}{\mu_\infty}}{S_2 \frac{\mu_{v_2}}{\mu_\infty}},$$

which reduces to

$$\pi = \frac{RT}{n_e e_0} \log \frac{S_1 \mu_{v_1}}{S_2 \mu_{v_2}}.$$

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[1] l. c.

From this it appears that in order to test the formula for the E. M. F. of the chain, the concentration of the salt solutions and the electrical conductivities of the latter are the only quantities that need be known. It is fortunate that u_x thus cancels out, for it is just the quantity that it is generally impossible to ascertain in the case of non-aqueous solutions.[1]

The metals employed in making up the galvanic chains measured are silver and cadmium. The solutions used are silver nitrate in pyridine and in acetonitrile and cadmium iodide in acetonitrile. These solutions were chosen because their electrical conductivities have been determined.

The cells measured and the results obtained are as follows:

1. $\overset{+}{\mathrm{Ag}}$ | *n*/10 $AgNO_3$ in pyridine | *n*/100 $AgNO_3$ in pyridine | $\overset{-}{\mathrm{Ag}}$ 0.035 volt.
2. $\overset{+}{\mathrm{Ag}}$ | *n*/10 $AgNO_3$ in pyridine | *n*/500 $AgNO_3$ in pyridine | $\overset{-}{\mathrm{Ag}}$ 0.061 volt.
3. $\overset{+}{\mathrm{Ag}}$ | *n*/10 $AgNO_3$ in pyridine | *n*/1000 $AgNO_3$ in pyridine | $\overset{-}{\mathrm{Ag}}$ 0.076 volt.
4. $\overset{+}{\mathrm{Ag}}$ | *n*/8 $AgNO_3$ in acetonitrile | *n*/128 $AgNO_3$ in acetonitrile | $\overset{-}{\mathrm{Ag}}$ 0.046 volt.
5. $\overset{+}{\mathrm{Cd}}$ | CdI_2 in acetonitrile | CdI_2 in acetonitrile | Cd 0.032 volt.
   (1 g-mol in 48.9 liters) (1 g-mol in 214.7 liters).

The apparatus used and the method employed in making the determinations have been previously described.[2] The measurements are accurate to one millivolt. In each case, after measuring the E. M. F. of the above chains, the electrodes were washed with distilled water, then thoroughly wiped with clean filter-paper and interchanged, after which the E. M. F. was again determined. The results thus obtained always agreed to within 0.001 volt. The silver electrodes were cut from one and the same piece of pure sheet silver. The cadmium electrodes were in the form of sticks and were made from one and the same stick of Schuchardt's C. P. cadmium.

In the formula

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[1] Compare the discussion in my previous article, l. c.

[2] Kahlenberg. l. c.

$$\pi = \frac{RT}{n_e e_0} \log \frac{S_1\mu_{v_1}}{S_2\mu_{v_2}},$$

$\frac{RT}{n_e e_0} = 0.058$, when $T = 290$, and $n_e = 1$, as in the case of silver. when $n_e = 2$, as in the case of cadmium, $\frac{RT}{n_e e_0} = 0.029$.

The molecular conductivities of the solutions used in the above chains are as follows:

AgNO$_3$ in pyridine[1] (at 25° C.)

V.	μ
10	24.7
100	31.57
500	41.8
1000	47.5 (extrapolated)

AgNO$_3$ in acetonitrile[2] (at 25° C.)

V.	μ
8	54.5
128	118.3

CdI$_2$ in acetonitrile[2] (at 25° C.)

V.	
48.9	33.7
214.7	37.7

The calculated E. M. F of the above chains are therefore as follows:

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[1] According to Lincoln. Trans. Wis. Acad. Sciences, Arts and Letters, 12, 395 (1899). Also Jour. Phys. Chem. 3, 457 (1899).

[2] According to Dutoit and Friderich. Bull. Soc. Chim. Paris, (3) 19, 321 (1898).

	Found
1. $0.058 \log \frac{0.1 \times 24.7}{0.01 \times 31.57} = 0.052$ volt	0.035 volt
2. $0.058 \log \frac{0.1 \times 24.7}{0.002 \times 41.8} = 0.085$ "	0.061 "
3. $0.058 \log \frac{0.1 \times 24.7}{0.001 \times 47.5} = 0.099$ "	0.076 "
4. $0.058 \log \frac{0.125 \times 54.5}{0.0078 \times 118.3} = 0.050$ "	0.046 "
5. $0.029 \log \frac{0.02045 \times 33.7}{0.0046576 \times 37.7} = 0.017$ "	0.032 "

The found voltages have been placed in the last column to facilitate comparison.

The utter disagreement between calculated and found values is at once apparent. Only in chain (4) do we have a tolerable agreement. It is to be noted that in this chain the solutions used are silver nitrate in acetonitrile and that the conductivity of these solutions is relatively high, approximating that of solutions of silver nitrate in water. The application of Nernst's formula to a chain like (4), in which water is used as a solvent, has also yielded satisfactory results.

To be sure, in calculating the E. M. F. according to the formula here used, the difference of potential at the junction of the two solutions has been neglected. Unfortunately, it is not possible to take this into consideration in the calculation,—as might be done by using Nernst's complete formula[1] — for the reason that data concerning the rate of migration of the ions in non-aqueous solutions have not been ascertained up to the present time. Still the change that the above calculated values would sustain by such a correction would no doubt be slight, as the E. M. F. at the contact of the solutions in question is very likely relatively small. Just what this E. M. F. at the contact of the solutions is, could, of course, be ascertained experimentally;

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[1] Compare LeBlanc, l. c.

but this would involve making up rather long galvanic combinations, the potential of which would be difficult to measure with a sufficient degree of accuracy, in most cases, at least, on account of the high resistance that non-aqueous solutions generally have.

The results here given show that Nernst's formula does not, in general, enable one to calculate the E. M. F. of concentration chains in which non-aqueous solutions are used. The single exception above noted, in which a tolerably satisfactory agreement between calculated and found values is obtained, is possibly a mere coincidence due to the fact that the conductivity of the non-aqueous solution approximates that of the aqueous solution in this case.

In the face of these facts and those presented in my previous article, it would be well to subject this formula to a more rigid test, even in the case of aqueous solutions. The electrical conductivity of non-aqueous solutions is being investigated further in this laboratory. As the results of these labors are obtained, they will be employed in testing further the formula here under consideration.

Laboratory of Physical Chemistry,
University of Wisconsin,
June, 1900.

SOLVENT ACTION OF VAPORS

BY A. T. LINCOLN

The existence of solid solutions has been thoroughly demonstrated and the study of liquid solutions, wherein one or both of the components may be a liquid, has been and still is a very considerable field of investigation. Since the solvent action is a function of the temperature and pressure and in general increases with the increase of the former, it seems hardly probable that this specific action which is manifested by the substance in the solid phase and more markedly in the liquid phase should become nil as soon as the vapor phase has been reached. Some attention has been devoted to the solvent action of substances in the vapor phase, and the object of this investigation is to see if some additional data could not be collected which would aid in the solution of this problem. We will first present the theoretical aspect of the subject and then give the experimental data which we have collected.

As the solubility is a function of the temperature and pressure, it will be necessary that the diagram employed will have to represent the effects of these two factors. Neither a simple temperature-pressure nor a temperature-concentration diagram will do it; but by means of a combination of these two, the resulting surface could be used to illustrate what we desire. Since, however, it introduces a solid figure, the complications which arise make the treatment rather difficult and confusing. The result may be reached in a simpler manner by a plain figure if we employ as our abscissæ the temperature, and as the ordinates the volume concentration. For illustration, let us take the simple case for water as given in Fig. 1. Since the density of water changes but slightly with the temperature, the portion of the curve, SPW, representing the solid phase of water, will be nearly horizontal as far as the melting-point M. Here there is a decided change in the density and the volume concentration increases, hence the break extends upward. The liquid phase portion of the curve LPW will gradually drop down until the critical point C is reached. For the volume concentration of the vapor phase of water, we shall have the curve VPW, which is very much lower than those for the liquid and solid phases.

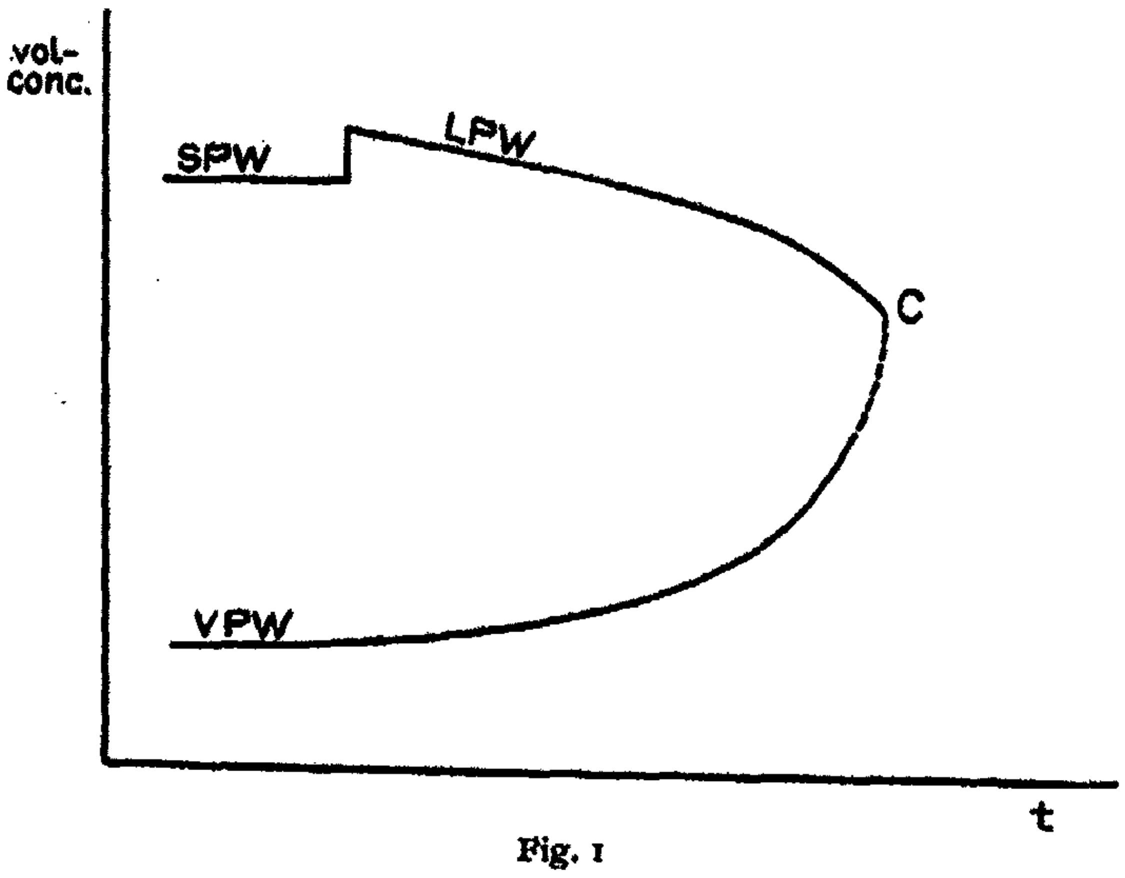

Fig. 1

Now let us consider the case of two pure components for temperatures below the critical point, say up to the melting-point of the higher melting substance. In Fig. 2 let SPA, LPA and VPA represent the curves for the volume concentration of the solid, liquid and vapor phases of A respectively. As a rule, the liquid phase is less dense than the solid; we will indicate this by a decrease of the volume concentration at the melting-point of the substance instead of an increase as in the case of water. In an analogous manner for the other component B, we will represent the relative volume concentration for the solid, liquid and vapor phases by the curves SPB, LPB and VPB respectively, the melting-points at M$_1$ and M$_2$, while C$_1$ and C$_2$ represent the critical points.

The volume concentration at some temperature, such as the eutectic temperature, we may designate by the location of E, then the volume concentration of pure A in the liquid phase for the temperatures between this and its own melting-point will be represented by the curve EM$_1$, while between the eutectic temperature and the melting-point of the other component B, by the curve EF. In a like manner we have the values for the

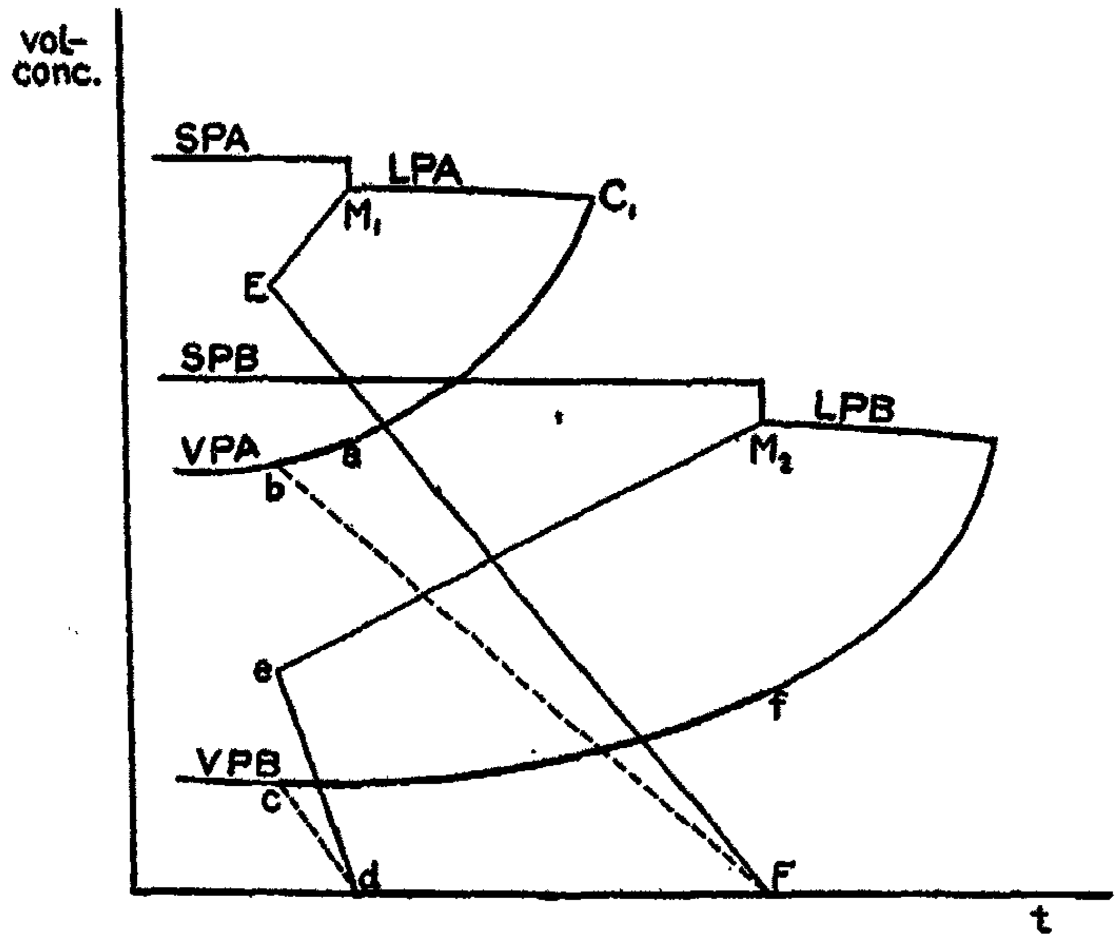

Fig. 2

volume concentration of pure B in the liquid phase between the eutectic temperature and the melting-point of the component A, represented by the curve *ed*, while the curve *e*M$_2$ represents the volume concentration between the eutectic point and the melting-point of B. For the components in the vapor phase we shall have the curve *ab* for the volume concentration between the melting-point of A and the eutectic temperature, while the curve *b*F represents it between the eutectic temperature and the melting-point of B; the curves *dc* and *cf* representing the corresponding values for B in the vapor phase.

In the preceding, we have been dealing with the pure components. Now let us consider the solvent action of the components and at temperatures ranging above the critical temperature. In Fig. 3 we will represent the solid, liquid and vapor phases of the two components A and B as was done in Fig. 2. This diagram differs from Fig. 2 in that the values for the lower melting substance in the solid and liquid phases are lower than those for the higher melting component, and this is the case generally, but the relative position of these two curves is immaterial.

Let us consider first the liquid phase. For A we would have between the melting-point of A and the eutectic tempera-ture the volume concentration represented by EM_1, while at the critical temperature of A there would be some of the component B present, and hence the volume concentration at the critical

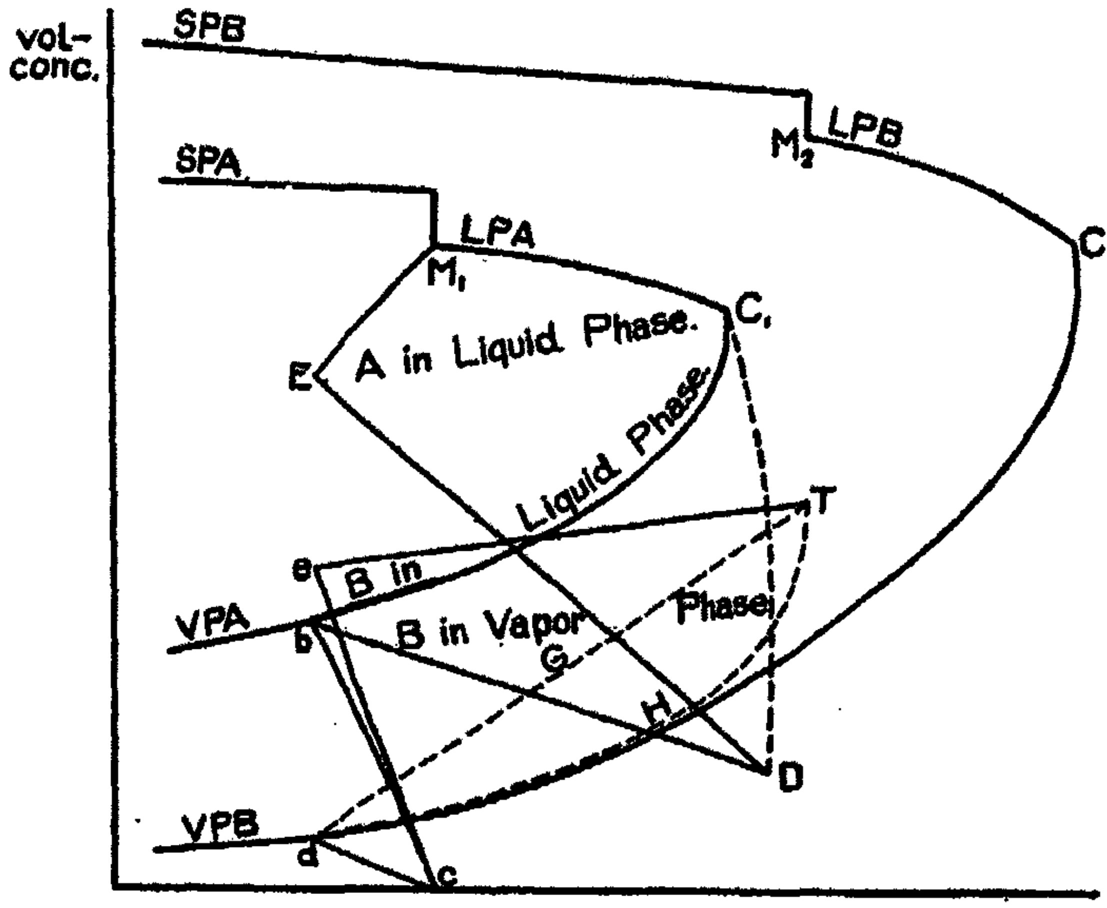

Fig. 3

temperature C_1 would be represented by some point as D, then the curve ED will represent the volume concentration of B from the eutectic temperature to the critical temperature of A, while the curve C_1D represents the limiting surface. In like manner for the component B in the liquid phase, the curve *ce* represents the volume concentration between the melting-point of A and the eutectic temperature, but for temperatures higher than this what direction will the curve take? This depends upon whether A above its critical temperature has any solvent action on B. It either has or it has not. If it has not, then the volume concentration of B above the critical temperature of A would lie in the line $VPBC_2$, and if it has a solvent action, it would lie above. As early as 1880 Hannay and Hogarth[1] showed that KI, KBr, and $CaCl_2$ were dissolved by alcohol vapor above its critical temperature. A solution of sulfur in CS_2 did not separate sulfur at 50° above the critical point, and selenium also remained in solution. Resin in some light paraffins remained in solution at 360°–100° above the critical point. And in the case of $CoCl_2$ in alcohol, the same characteristic absorption bands were present at 300° as at 15°. Further, they showed that the decomposition-product of chlorophyll by acids gave the same characteristic bands in alcoholic vapor at 350° as in alcoholic solution. Villard[2] has shown that iodine is dissolved by CO_2 above the critical point and that the absorption spectra of the vapor does not show the least characteristic of gaseous iodine. Even at 20°–25° there was an appreciable coloration of the CO_2, due to the iodine dissolved. That vapors manifest a solvent action has also been shown by Pictet.[3] Wood[4] demonstrated that iodine and bromine are soluble in CS_2 above its critical temperature and confirmed the work of Hannay and Hogarth concerning the solubility of KI in alcohol vapor. He further showed that HgI_2 is soluble in ether vapor.

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[1] Proc. Roy. Soc. 30, 178 (1880).

[2] Comptes rendus, 120, 182 (1895).

[3] Ibid., 120, 64 (1895).

[4] Phil. Mag. 41, 423, (1896).

From the experimental results just considered, we see that above the critical temperature many substances do manifest a solvent action. Now referring to Fig. 3 again, we will locate that point above the critical temperature at T, thus showing that the quantity of the component B present is more than would be represented by the curve $VPBC_2$ at that particular temperature, i. e., some has been dissolved.

Now considering the concentration in the vapor phase in a manner analogous to that employed for Fig. 2, we see that the curve *ab* represents the volume concentration of A between the melting-point of A and the eutectic temperature, while *b*D represents it up to the temperature where A ceases to exist as a liquid. For the component B, the curve *cd* represents the volume concentration between the temperature of the melting-point of A and the eutectic temperature. If the vapor of A does not exert any solvent action, then the point will fall on the line VPB, but we do not know whether it does or whether it does not at this particular temperature, but at this low temperature, these values must approximate each other so closely that at some temperature they may be considered as identical. Then the curve which represents the volume concentration between the temperature represented at *d* and T must pass through these two points. Whether this boundary curve takes the directiou *d*GT or *d*HT, we do not know; but it is presumable that the change in the concentration will fall off much more rapidly at the higher temperatures than at the lower, and therefore *d*HT would be the more probable curve, and hence the volume concentration curve would drop rapidly until it came near the vapor pressure curve for pure B and would no doubt approach it asymptotically. Hence we see that in order to determine whether the vapor has a solvent action and to measure this, it would be necessary to work at the higher temperatures where the curves *d*HT and $VPBC_2$ are some distance apart. In other words, we would have to work at such temperatures where the difference between the partial pressure and vapor pressure of one component was greater than the experimental error.

It was hoped by choosing salicylic and benzoic acids that we had substances which would give us vapors, the composition of which could be readily determined and at the same time, that the difference between the partial pressure and the vapor-pressure would be much greater than the experimental errors. The presentation of the experimental part will now be given.

As the vapor pressure of salicylic and benzoic acids could not be found in the literature, it was necessary to determine these values for the lower temperatures at least. The method employed was substantially the same as that used by Ramsay and Young.[1]

The acids were fused upon the bulb of a standardized thermometer and this placed into a 100 cc distilling flask and then heated by means of an oil-bath. The bath was kept at 30°–40° above the temperature recorded by the thermometer in the distilling flask. When the flask was immersed directly into the bath, the vaporization of the acids was not sufficiently rapid to keep the temperature constant and consequently the difference between the readings of the two thermometers would be only a few degrees. By this method it was impossible to raise the temperature of the bath much above the temperature registered by the thermometer of the flask. In order to get the temperature of the bath sufficiently high above that of the thermometer within the flask it was found necessary to place the flask into a small beaker and pack cotton batting tightly around the flask, thus making an air-bath. The beaker with its contents was then immersed nearly to its top in the oil. By this modification, we were able to keep the bath at any desired temperature above that recorded by the thermometer in the flask.

This flask was connected with a manometer which read to millimeters and this in turn with a Boltwood mercury pump. All joints were made by fusing the glass tubes together, except two,— the connection with the mercury pump, which was a mercury joint and the rubber stopper through which the thermometer, on which was the fused acid, passed into the distilling

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[1] Phil. Trans. 175, 37 (1884).

flask. This latter joint was made tight by pressing the stopper below the top of the neck of the flask and sealing by means of a mixture of beeswax and rosin. With the connections made in this manner, and all of the stop-cocks well greased with a lubricant consisting of pure India rubber and beeswax, any pressure desired could be obtained and retained for hours.

With the apparatus in this form, the vapor pressures of salicylic and benzoic acids were obtained. The values are given in Tables I. and II. respectively. In the first column is given the temperatures as read from the thermometers, while the corrected values are given in the second column. These corrections are the corrections which are due to the portion of the thermometer thread which is exposed to the air and which extends outside of the flask. The corrections were made from the table as given in Landolt and Börnstein's Tabellen. In the last column is given the pressure in millimeters of mercury.

Table I

Vapor Pressure of Salicyclic Acid

Temperature		Pressure mm.
Observed	Corrected	
82.5°	82.5°	0.3
86.6	86.6	0.5
103.2	103.2	1.0
103.4	103.4	1.0
115.4	116.1	2.0
114.2	115.0	2.5
115.2	115.9	2.5
121.2	122.1	3.0
131.2	132.2	6.5
137.0	138.2	11.0
139.0	140.3	11.5
139.5	140.8	12.0
147.0	148.6	21.0
145.4	146.9	22.5
149.2	150.9	27.0
153.2	155.0	37.0
155.0	156.9	44.0

TABLE II

Vapor Pressure of Benzoic Acid

Temperature		Pressure mm.
Observed	Corrected	
71.3°	71.3°	0.2
70.8	70.8	0.4
92.0	92.0	1.0
99.0	99.0	1.8
101.6	101.6	2.0
107.0	107.0	3.0
109.8	110.3	3.2
118.0	118.8	5.5
131.3	132.3	11.0
145.4	146.9	21.5
147.3	148.9	23 0
153.3	155.1	30.5
153.9	155.8	31.2
158.8	160.8	40.0
160.2	162.3	41.0
165.0	167.4	50.0
165.1	167.5	51.0
169.0	171.4	60.2
169.8	172.2	62.2
172.8	175.4	71.0
172.9	175.5	70.5
176.0	178.7	80.0
176.0	178.7	80.5
179.2	181.9	91.0
182.0	184.8	101.0
182.1	184.9	103.0
185.3	188.2	115.0
187.6	190.5	127.5
187.7	190.6	126.0
190.0	193.0	136.0

In Fig. 4[1] will be found a graphical representation of the vapor pressures of these two acids. The temperatures are plotted along the abscissæ and the logarithm of the pressures along the ordinates.

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[1] The value marked K is plotted from a value determined by Kahlbaum. Since there is a decided break in the vapor-pressure curve of benzoic acid and the vapor condenses in the neck of the flask, this would make a very good laboratory experiment.

It will be noticed that the values for salicylic acid are very much higher than required by the curve prolonged. This is no doubt due to the experimental difficulty in reading the low pressures by means of a mercury manometer graduated to millimeters. The same is true for the first few values given for benzoic acid.

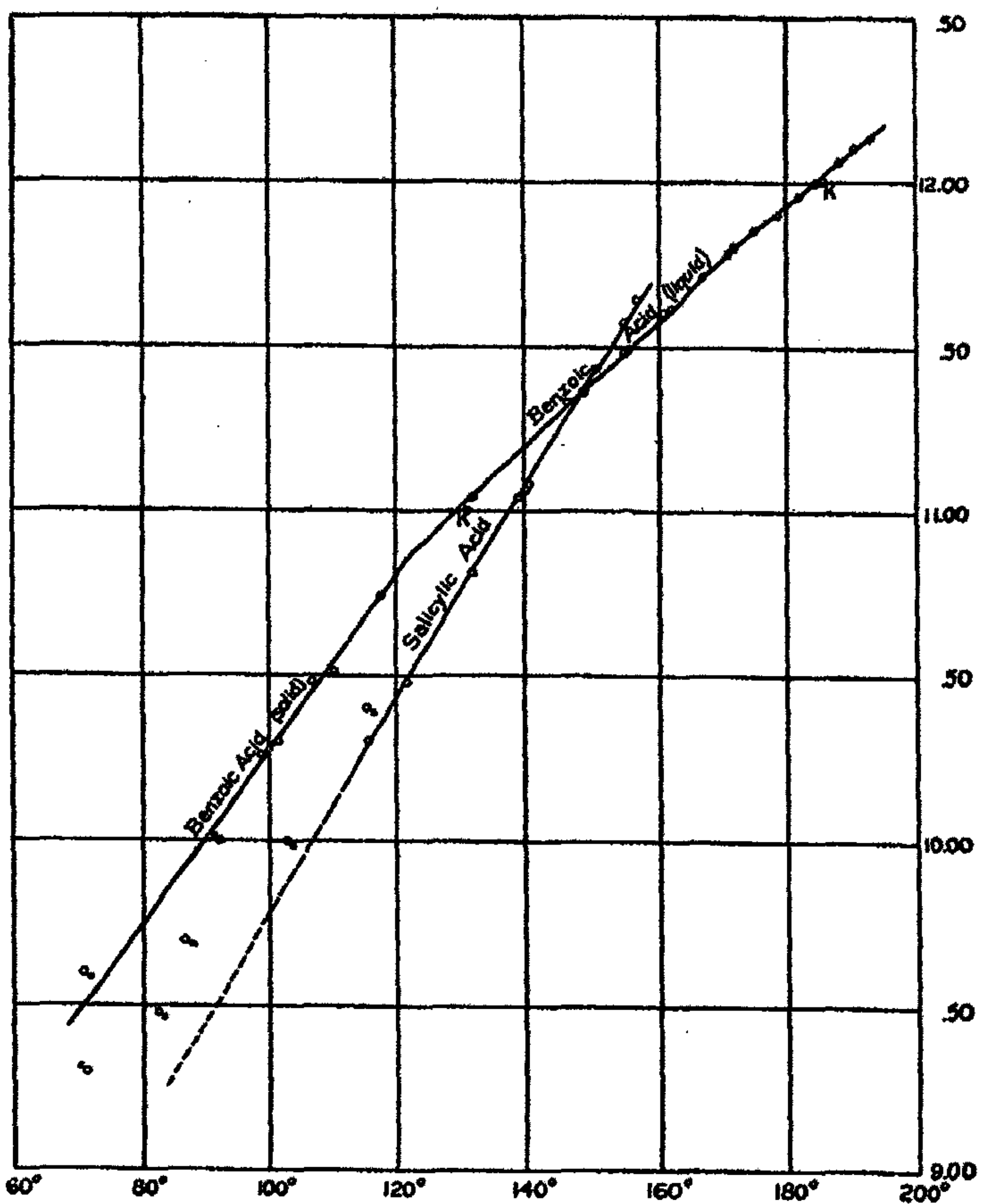

Fig. 4

The distillation of the saturated solutions was carried out by placing in a retort considerably more of the solute than would be dissolved by the solvent at the temperature of the experiment. Since solubility determinations are not given, this had to be determined experimentally. The mixture was then boiled by usually heating the retort in a glycerol bath, but it was found that it was immaterial whether the heat was supplied in this manner or by direct flame since the distillate contained practically the same per cent of the solute. In order to prevent condensation on the neck of the retort and to insure that all of the vapor—both of the solute and solvent—was carried over, the neck of the retort was heated electrically. When water was used as solvent, it was found that considerable of the solute would separate in the solid phase when the distillate was cooled. So in order to be sure that all of the distillate was collected in the receiving flasks it was necessary that all of the condensation should take place in the flasks. Hence these flasks were surrounded by ice and successive portions of the distillate collected in different flasks. Considerable difficulty was, however, experienced when it was necessary to distil under diminished pressure. In order to collect different portions and at the same time have the condensation take place in the receiving flask, a Y-tube was placed on the end of the delivery tube, and on the two ends of this tube were placed two small flasks. When a sufficient quantity of the distillate had been collected in one of them, the ice-bath was removed and the tube rotated so that the two flasks would exchange places and then this second flask was surounded by the ice and the distillate collected in it.

These particular substances were chosen for experimentation so that it would be a simple matter to analyze the distillates for the acids by titrating with a standard alkaline solution. For this purpose about a *n*/50 solution of barium hydroxide was prepared; but it was not an easy matter to find a suitable indicator. For the analysis of salicylic acid in water, acetone and benzol solutions, Walker and Wood[1] recommend the use of Congo-red as an efficient indicator. My experience, however, with the particular sample of Congo-red used, was very unsatisfactory. In exceedingly dilute solutions the end reaction is apparently fairly delicate, but in moderately concentrated warm aqueous solutions the end reaction is not sharp, but there is a gradual transition in color and no distinct change on which to set.

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[1] Jour. Chem. Soc. 73, 619 (1898).

Several other indicators were tested and the results for phenolphthalein and paranitrophenol are given in Table III.

TABLE III

Salicylic Acid in Aqueous Solutions
Indicator — Paranitrophenol

	Grams of acid		
	Taken	Found	Percent
1	0.229	0.2284	99.72
2	0.202	0.1957	96.9

Indicator — Phenolphthalein

1	0.1624	0.1630	100.3
2	0.2161	0.2175	100.6

Walker and Wood state that they did not find phenolphthalein to give good results.

For the determination of benzoic acid in aqueous solutions, rosolic acid was used as an indicator and the preliminary determinations gave the following results:

	Grams of acid		
	Taken	Found	Percent
1	0.0321	0.03207	99.9
2	0.0596	0.05935	99.7
3	0.0915	0.09165	100.2

In benzol solutions of benzoic acid, it was found that by adding the barium hydroxid solution direct the indicator used was more soluble in the water layer, and by rather vigorous shaking the coloration imparted to the aqueous layer could be used as the criterion upon which to determine the end of the reaction. Hence the titrations can be made by running the alkaline solution direct into the benzol solution and setting on the change of color of the aqueous layer. In Table IV. are given the results of the preliminary experiments.

TABLE IV

Benzoic Acid in Benzol

Indicator — Rosolic Acid

	Grams of acid		
	Taken	Found	Percent
1	0.0468	0.04689	100.2
2	0.0394	0.03978	101.0
3	0.0286	0.02843	99.4

Indicator — Paranitrophenol

1	0.0395	0.03963	100.3
2	0.0275	0.02723	99.0
3	0.0375	0.03782	100.7

Paranitrophenol can be used with about as fair a degree of accuracy as rosolic acid provided one sets on the appearance of the canary yellow coloration, i. e., on the color of the aqueous solution of paranitrophenol.

Rosolic acid was used as the indicator in the analyses of the distillate of both the aqueous and benzol solutions of benzoic acid.

Acetone was first employed as solvent for salicylic acid, but owing to its low boiling-point, a mere trace of the acid was found in the distillate. Water was next employed, but upon distilling a saturated solution of salicylic acid, a distinct odor of phenol was detected and upon further examination, it was found that carbon dioxid was given off. Although considerable salicylic acid was detected in the aqueous distillate as well as in the distillate from benzol solutions, it was advisable owing to the unfavorable action of the acid to devote our attention to benzoic acid.

In preparing a saturated solution of benzoic acid in water, it was found that two liquid layers were formed before the temperature of the boiling-point of the mixture was reached. The distillate was collected in the manner described above, and two determinations were made under diminished pressure, with the aqueous solutions. In Table V. is given the results of these determinations. In the first column is the pressure under which the vaporization took place, and in the second column is the temperature of the boiling mixture. The third column contains the percent of benzoic acid in the distillate, while the next to the last column contains the partial vapor pressure due to the benzoic acid in the distillate. The value of this partial pressure was calculated, from the following formula:

$$\frac{\frac{g_1}{M_1} \cdot P}{\frac{g_1}{M_1} + \frac{g_2}{M_2}} = p,$$

where g_1 is the number of grams of the solute in one hundred grams of the distillate, and g_2 the number of grams of solvent. Whereas M_1 and M_2 represent the molecular weights of the solute and solvent respectively, P represents the total pressure of the distillate, and p the partial pressure due to the vapor pressure of the solute. In the last column appears the vapor pressures of the pure solvent at the respective temperatures, as interpolated from Fig. 4.

TABLE V

Benzoic Acid

Solvent — Water

Pressure mm.	Temp.	Pct. acid	Vapor-pressure of solute	
			Found	Theory
587	91.4°	0.832	0.7	1.1
628	94.6	1.275	1.2	1.3
735	99.6	0.965	1.2	1.8
735	99.6	1.040	1.1	1.8
741.6	99.8	1.023	1.1	1.85
741.6	99.8	1.032	1.1	1.85
745.7	100	1.027	1.1	1.87
745.7	to 120.0	1.376	1.5	—
746.4	100.4	0.946	1.0	1.9
746.4	100.6	1.058	1.2	2.0
746.4	100.8	1.108	1.2	2.0
746.4	101.1	1.144	1.3	2.0

Some difficulty was experienced in preparing a saturated solution of benzoic acid in benzol under atmospheric pressure owing to the great solubility of the acid in this solvent. By the addition of benzoic acid, the boiling-point of benzol was raised about thirty-six degrees and yet the solution was apparently not saturated. Therefore saturated solutions were prepared under diminished pressure, the distillates collected and analyzed and in Table VI. are given the results thus collected. The columns have the same respective significance as in the preceding table.

TABLE VI
Benzoic Acid
Solvent — Benzol

Pressure mm.	Temp.	Pct. acid	Vapor-pressure of solute	
			Found	Theory
542	104–6°	0.537	2.0	2.5
590	102–5	0.389	1.5	2.4
606	86–88	0.150	0.6	0.85
606	89	0.177	0.7	0.96
613	94–95	0.264	1.0	1.3
623	101–4	0.405	1.6	2.1
632	94–96	0.290	1.2	1.4
633	98–100	0.320	1.3	1.8

From an examination of the results given in Tables V. and VI., it will be readily observed that the partial pressure due to the solute, benzoic acid, is approximately equal to the pressure which this substance would exert if it were in the free condition at the respective temperatures. In other words, the values of the partial pressure for benzoic acid and for its vapor pressure are within the limit of expermental error, and therefore as in Fig. 3, represent that portion of the curves for the volume concentration at that range of temperature where they lie very close together. Hence, in order to prove whether these solvents exert any solvent action when in the vapor phase, upon benzoic acid, it would be necessary to conduct the experiments at a much higher temperature.

That the same is also true concerning the solvent action of ethyl alcohol vapor toward camphor and methyl alcohol becomes apparent from a comparison of the partial pressure of these substances in the distillate from saturated alcoholic solution and determined experimentally by Talmadge,[1] and the vapor pressures of these substances as recently published by Allen.[2] In Table VII. will be found in the first column the temperatures at which the distillate passed over, in the second column the partial pressures as determined experimentally by Talmadge and calculated in the manner described above, while in the last column is given the values of the vapor pressures of camphor and naphthalene as interpolated for these particular temperatures, from the determinations by Allen.

TABLE VII

Ethyl Alcohol Solutions

Camphor

Temp.	Pressure in mm.	
	Found	Theory
71°	3.4	4.6
86	6.7	9.2[3]

Naphthalene

Temp.	Found	Theory
51°	0.7	0.8
56	1.2	1.3
57	1.3	1.5
59	1.6	1.7
60	1.7	1.8
66	2.6	2.8
67	2.8	3.0

As in the case of benzoic acid, camphor and naphthalene give values for their partial pressures, which are slightly under the values of the vapor-pressures of these substances at

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[1] Jour. Phys. Chem. 1, 547 (1897).

[2] Jour. Chem. Soc. 73, 411, 415 (1900).

[3] At 80°.

the respective temperatures, all of which are within the limit of experimental error.

The results presented in the preceding pages may be summarized as follows:

1. The coordinate system volume concentration and temperature has been employed to represent the concentration, pressure and temperature effects.

2. It has been pointed out that theoretically the vapor should have a solvent action; but whether this is demonstrable experimentally depends upon whether the difference between the partial pressure and the vapor pressure of the component called the solute is greater than the experimental error. And only at high temperatures in the vicinity or above the critical point of the solvent is this probably the case.

3. The distillate from saturated aqueous, benzol and acetone solutions of salicylic and benzoic acids contains some of these acids; but the quantity present exerts a partial pressure about equal to the vapor pressure of the pure solute and the difference is within the limit of error. This is also true for camphor and naphthalene in vapors of ethyl alcohol.

4. The vapor pressure data for salicylic and benzoic acids over a range of temperature for about 70° to 190° have been presented.

In conclusion, I desire to express my gratitude to Professor Bancroft for his assistance during this investigation.

Cornell University,
June, 1900.

NEW BOOKS

Le Fluor et ses Composés. *By Henri Moissan. 17 × 25 cm.; pp. xii + 396 Paris: G. Steinheil, 1900.* — In this handsome volume, Moissan has given us a monograph on fluorin and its compounds. In this particular case, the value of the book is much increased by the fact that Moissan has himself made so many of the discoveries which he describes; but the volume would be a necessity to chemists even had it been written by one less identified with the subject. The text-books cannot go into matters in great detail, owing to lack of space. Therefore we must have monographs unless we are to be content with a hopelessly superficial view of our subject. It is much to be desired that we should have more monographs and that they should be written by the most competent authorities. This book is to be welcomed for what it is and also for that which it typifies.

The reviewer has been much interested by Moissan's statement, in the preface, in regard to one aim of modern chemistry: "The important point would be to be able to transform simple substances of the same group, as we now transform the allotropic forms of a single element." This is very true, but it suggests the question whether it would not be well to study the allotropic forms of the elements more carefully than has yet been done. The recent work of Saunders on the allotropic forms of selenium shows how little was really known about that element, while the discovery of the rapid change of one form into another in presence of certain organic liquids suggests the possibility of similar changes among the elements. If we could explain why certain liquids act as they do on amorphous selenium, we should have made a long stride toward discovering the conditions under which a mutual transformation of the halogens becomes possible.

Wilder D. Bancroft

Die Fortschritte der Physik. *Dargestellt von der physikalischen Gesellschaft zu Berlin. In Jahre 1899. Erste Abtheilung: Physik der Materie; redigirt von Richard Börnstein und Karl Scheel. pp. lxxvii + 693; 16 × 23 cm. Braunschweig: Friedr. Vieweg und Sohn, 1899. Price: paper 26 marks.* — With the present large volume, the *Fortschritte* for last year (1899) begins to appear. Now that this important publication has been brought up to date, the German Physical Society, in whose charge it is issued, recalls that the original plan was to publish prompt and complete yearly reports of the literature of physics; that, in the actual execution, the completeness was attained at a sacrifice of the promptness, until the reports had fallen six years behind; and that this state of affairs led to a reorganization of the editorial methods in 1892, with the result of making up all the lost time. It is now understood that the work is to continue to appear promptly year by year, which will add greatly to its value and yet more to its interest. The present volume, on the 'Physics of

Matter', pays the usual attention to physical chemistry, forty-two percent of the whole being devoted to this subject—not reckoning the eighty-eight pages on the work of the year in crystallography.

J. E. Trevor

Theoretische Chemie vom Standpunkte der Avogadro'schen Regel und der Thermodynamik. *By Walther Nernst. Third Edition. 16 × 26 cm.; pp. viii + 696. Stuttgart: Ferdinand Enke, 1900.*—The third edition of this work follows closely on the heels of the second (3, 337). The only changes are a page here and there, so that a detailed consideration is superfluous.

Wilder D. Bancroft

Lectures on Theoretical and Physical Chemistry. *By J. H. van 't Hoff. Translated by R. A. Lehfeldt. Part II.: Chemical Statics. 15 × 23 cm.; pp. 156. London: Edward Arnold. Price: cloth, 8s.6d. net.*—It is wit pleasure that attention is called to the English translation of the second part of van 't Hoff's lectures (3, 497).

Wilder D. Bancroft

Leçons de Chimie physique, *professés a l'Université de Berlin. Par J. H. van 't Hoff. Ouvrage traduit de l'allemand, par M. Corvisy. Troisième partie. Relations entre les Propriétés et la Composition. 17 × 25 cm.; pp. ii + 170. Paris: A. Hermann, 1900. Price: paper, 7 francs.*—Translating and printing seem to be done more rapidly in France than in England, for the third portion of van 't Hoff's lectures (4, 396) has now appeared in French.

Wilder D. Bancroft

La Garance et l'Indigo. *By George F. Jaubert. (Encyclopédie scientifique des Aide-Mémoire.) 12 × 19 cm.; pp. 166. Paris: Gauthier-Villars. Price: paper 2.5, boards 3 francs.*—Artificial madder has driven out the natural product completely, and the author is of the opinion that the natural indigo will soon be supplanted by the synthetic compound. We are therefore given a short monograph on the development and present state of the two industries.

Wilder D. Bancroft

NAME INDEX

to Papers and Reviews

NAME INDEX

to New Books

SUBJECT INDEX

Exclusive of New Books