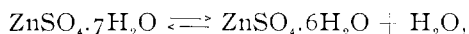


ON THE INVERSION OF THE HEPTA- AND HEXA- HYDRATES OF ZINC SULPHATE IN THE CLARK CELL

BY H. T. BARNES

The change in the hydration of zinc sulphate,



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. Jaeger⁴ was published which

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 ₂ SO ₄	ZnSO ₄	Zn	(Clark)
Hg	Hg ₂ SO 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

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

Jaeger and Wachsmuth¹ to occur at about 5°, and subsequently shown by Kohnstamm and Cohen² 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

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" cell¹ 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

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

$$R_1 = \frac{(e - E - 20)r}{20}.$$

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

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 $1/10^{\circ}$.

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.

¹l. c., p. 149.

TABLE I

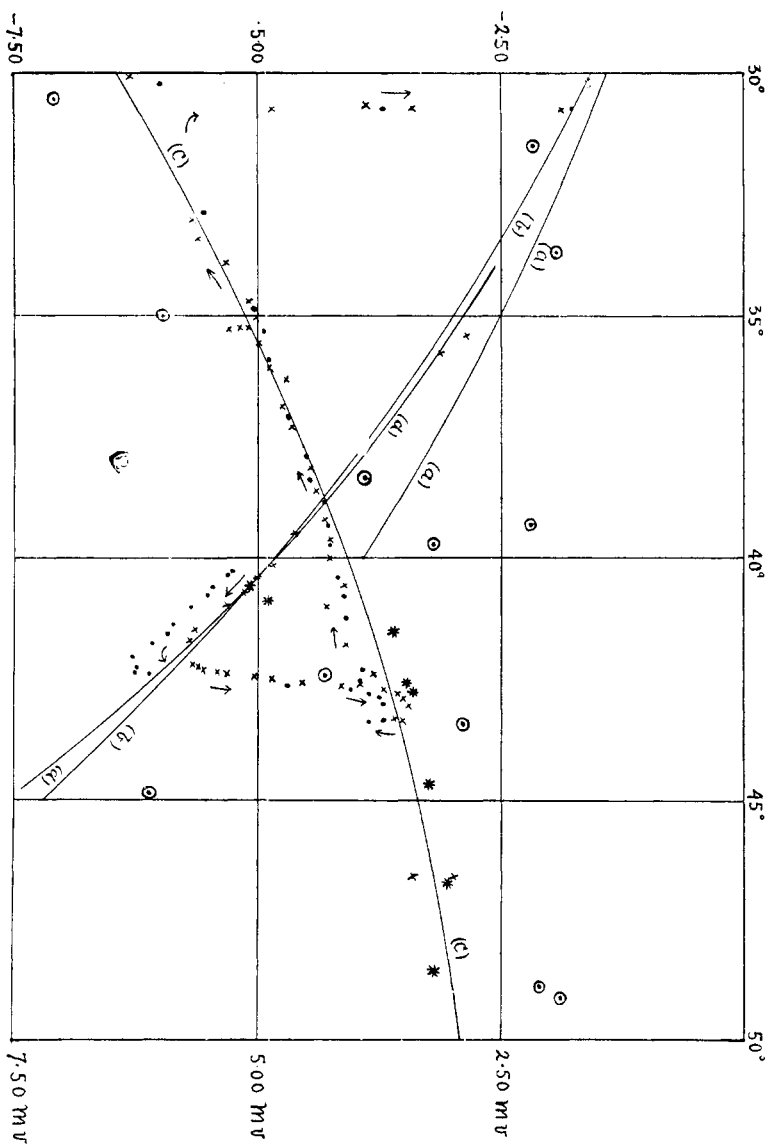
Temp C	Observed change in mv from 15° C	Calculated by linear formula	Difference
40.60	-35.81	-30.72	-5.09
30.14	19.78	18.17	1.61
30.32	20.00	18.38	1.62
35.44	27.39	24.53	2.86
42.58	36.56	33.10	3.46
46.74	41.14	38.09	3.05
48.58	43.50	40.30	3.20
35.79	28.08	24.95	3.13
40.09	34.99	30.11	4.88
42.79	36.76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

$$E_t - E_{15} = 1.200 (t - 15)$$

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

¹ l. c. p. 151.



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 $-1.20(t - 15^{\circ})$
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

$$E_t - E_{15} = -1.200(t - 15^{\circ}) - 0.0062(t - 15^{\circ})^2 \dots (a)^1$$

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

$$-0.00006(t - 15^{\circ})^3 \dots \dots \dots (b)$$

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

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

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

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

The expression for the hexahydrate branch may be given

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

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

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°	$-1.20(t - 15^\circ)$	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

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

The extrapolated formula given by Jaeger is

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

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

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

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

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 pro-

duced. 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 deter-

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

minations between 0° and 50° are reproduced. The weight of salt p is here expressed in percent of solution.

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

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

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

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

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

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