[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

Crystal Perfection of $ZnSO_4 \cdot 7H_2O$. Partial Molal Heat Capacity, Heat Content and Vapor Pressure of its Aqueous Solutions. Thermodyanmics of Clark Cell[1]

BY W. F. GIAUQUE, R. E. BARIEAU AND J. E. KUNZLER

In a previous paper, Barieau and Giauque[2] have combined low temperature heat capacity measurements on zinc sulfate heptahydrate with the temperature coefficient of the Clark cell at 25°, and other data, for the purpose of investigating the crystal perfection of $ZnSO_4 \cdot 7H_2O$. If the entropy of the substance approaches zero at low temperatures there must be no disorder in the crystal. The work is connected with an investigation of low temperature magnetic properties of hydrated sulfates of the first transition series.

We are particularly interested in the problem of crystal perfection near 1°K. because this is a region of great interest in the study of magnetic phenomena. Randomly placed hydrogen bonds, or other types of disorder, may well exist as a matter of thermodynamic equilibrium at higher temperatures, and yet the system may become perfectly ordered at low temperatures in conformity with the equilibrium requirements of the third law of thermodynamics. However, if the ordering process requires that large potential barriers be surmounted, the rate may become so slow that the system cools to a false equilibrium at low temperatures.

Any attempt to interpret the results of magnetic and thermodynamic investigations on the assumption that a clean cut set of quantum levels exists in a system of well separated paramagnetic ions will meet difficulty if the electric fields about the ions involve matters of chance.

$ZnSO_4 \cdot 7H_2O$ is diamagnetic. Thus, its heat capacity is not complicated by the low lying energy levels of the paramagnetic members of the group. For this reason it has been investigated to find if this member of the first transition series attained crystal perfection at low temperatures.

The e. m. f. of the Clark cell changes considerably with temperature due, in part, to the changing solubility of $ZnSO_4 \cdot 7H_2O$ and the consequent change in the properties of the saturated solution. It was decided to measure the relative partial molal heat content and heat capacity of zinc sulfate solutions, so that the e. m. f. data on the Clark cell could be examined on a point by point basis, without the necessity of drawing tangents on a plot of e. m. f. against temperature.

Material Used and Method of Analysis.—The solutions were prepared from Baker C. P. $ZnSO_4 \cdot 7H_2O$. The concentration of the initial solution was determined by slow evaporation and dehydration of the samples as described in the previous paper.[2] The anhydrous material was finally heated to a constant weight at about 490°. This required about 4 days at this temperature. The concentrations of the more dilute solutions were calculated from accurate additions of water from a weight buret.

Method of Measurement.—The calorimeter used for the measurement of relative partial molal heat content and partial molae heat capacity was a considerably modified version of the ones used by Randall and Rossini[3] and Randall and Taylor.[4] It made use of the thermometer heater arrangement of Giauque and Archibald.[5] This modified calorimeter has been in used in this Laboratory for some time in a study of the partial molal properties of sulfuric acid solutions. It will be described in detail, in that connection, when the work on sulfuric acid solutions has been completed.

The Relative Partial Molal Heat Content of Aqueous Solutions of Zinc Sulfate.—A solution containing 15.6570 moles of water per mole of $ZnSO_4$ was placed in the calorimeter. The heat capacity of the calorimeter plus the solution was measured at about 35 and 27°. From the temperature coefficient of heat capacity the results could be computed to exactly 35 and 25°. Heat capacity measurements at 25 and 35° were then made after additions of water.

The results are summarized in Table I.

TABLE I

HEAT OF DILUTION OF ZINC SULFATE SOLUTIONS

Moles H_2O added per mole $ZnSO_4$	Total moles H_2O per mole $ZnSO_4$	Heat evolved, cal.	Av. relative partial molal heat content, cal. mole^{-1}, over interval
.....	15.6570	.....	.....
0.9401	16.5971	128.42	−136.6
5.1258	21.7229	325.49	−63.5
8.0173	29.7402	193.22	−24.1
10.6606	40.4008	115.13	−10.8
14.6064	55.0072	57.84	−3.96

Lange, Monheim and Robinson[6] have measured heats of dilution at concentrations below 1 molal, and have tabulated the relative partial molal heat contents of water, $\overline{L}_1$, and zinc sulfate, $\overline{L}_2$.

The results in Table I were used to draw a curve which joined smoothly with the data of Lange, Monheim and Robinson[6] and satisfied the average values of $\overline{L}_1$ over the intervals given in Table I.

Values of $\overline{L}_1$ were then read from the curve at various concentrations. The results are given in Table II. Values of $\overline{L}_2$ are also given in Table II. They were calculated by means of the Duhem equation

$$\overline{L}_2 - \overline{L}_{2(1\,M)} = -\overline{L}_1 A + (\overline{L}_1 A)_{(1\,M)} + \int_{A\,=\,55.51}^{A} \overline{L}_1\, dA \qquad (1)$$

where A represents the number of moles of water per mole of zinc sulfate. The values of the solubil-

---

(1) This work was supported in part by the Office of Naval Research, United States Navy.

(2) Barieau and Giauque, THIS JOURNAL, **72**, 5676 (1950).

(3) Randall and Rossini, *ibid.*, **51**, 323 (1929).

(4) Randall and Taylor, *J. Phys. Chem.*, **45**, 959 (1941).

(5) Giauque and Archibald, THIS JOURNAL, **59**, 561 (1937).

(6) Lange, Monheim and Robinson, *ibid.*, **55**, 4733 (1933).

TABLE II

RELATIVE PARTIAL MOLAL HEAT CONTENT, CAL. MOLE^{-1}, OF ZINC SULFATE SOLUTIONS AT 25°

A, moles H_2O per mole $ZnSO_4$	$-\bar{L}_1$	$-\bar{L}_1A$	$\bar{L}_2$	Remarks
55.506	(2.76)	(153)	(1443)	From L. M. and R.[6] H. and O.[8]
55	2.8	154	1445	
50	3.2	160	1466	
45	4.4	198	1523	
40	6.7	268	1620	
35	10.4	364	1758	
30	16.0	480	1940	
28	19.0	532	2026	
26	22.8	593	2129	
24	28.0	672	2259	
22	36.0	792	2442	
21.536	43.0	...	..	Satd. 0°
20.178	47.5	...	..	Satd. 5°
20	49.0	980	2713	
19	60	1140	2927	
18.966	60	...	..	Satd. 10°
18	77	1386	3241	
17.801	81	1442	3313	Satd. 15°
17.052	102	1739	3678	Satd. 18°
17	103	1751	3695	
16.657	115	...	..	Satd. 20°
16.5	120	1980	3980	
16	141	2256	4321	
15.598	163	2543	4669	Sard. 25°
15.5	169	2620	4763	Supersatd.

ity, used in Table II, were taken from Seidell.[7] A very small correction has been applied to make them consistent with the molecular weight of 161.44 used here. Harned and Owen[8] and Harned[9] have used e. m. f. data as a basis for a re-extrapolation of $\bar{L}_2$ as given by Lange, Monheim and Robinson,[6] in order to bring the limiting slope into agreement with the Debye–Huckel theory. They suggest lowering all values of $\bar{L}_2$ (L.M.R.) by 25 cal. mole^{-1}. We have applied this correction to all values of $\bar{L}_2$ given in Table II.

The Partial Molal Heat Capacities of H_2O and $ZnSO_4$.—The heat capacity measurements mentioned in the above section included the heat capacity of the calorimeter as well as the solution. In separate experiments, various amounts of water were placed in the calorimeter and heat capacity measurements were made. In this way the water equivalent of the calorimeter was determined. As would be expected, it was found that this quantity increased slightly with increasing amount of water in the calorimeter. The heat capacity of water was taken from the work of Osborne, Stimson and Ginnings.[10] When their data were converted to the defined calorie, the heat capacity of water was found to be 0.9989 cal. deg.$^{-1}$ g.$^{-1}$ at 25° and 0.9986 cal. deg.$^{-1}$ g.$^{-1}$ at 35°. The heat capacity of the calorimeter ranged from about 5% of the heat capacity of the most concentrated solution to about 3% of the most dilute solution. Since the vapor pressure of water above the zinc sulfate solutions could be calculated, a very small heat correction ranging up to several hundredths of a per cent. was made for vaporization during the temperature rise. The data are given in Table III.

TABLE III

HEAT CAPACITY OF AQUEOUS SOLUTIONS OF ZINC SULFATE

Wt. % $ZnSO_4$	*t*, °C. average	C_p, cal. deg.$^{-1}$ g.$^{-1}$
36.400	34.56	0.6656
36.400	35.09	.6662
36.400	34.26	.6645
36.400	26.76	.6561
36.400	26.78	.6567
29.204	24.90	.7103
29.204	34.76	.7210
23.154	24.43	.7601
23.154	33.52	.7693
18.154	24.95	.8065
18.154	34.40	.8123
14.008	25.93	.8460
14.008	33.92	.8515
11.005	26.11	.8775
11.005	34.17	.8784

The data in Table III were used to obtain values of C_p at 25 and 35°. The values at each temperature were then plotted as a function of concentration in various ways in an attempt to find a purely empirical equation which could be used for interpolation purposes. Rossini[11] has shown that a plot of C_p (apparent) against $1/A^{1/2}$ represents the data of uni-univalent electrolytes rather well.

The apparent molal heat capacity of $ZnSO_4$, C_p (app.), was calculated by means of the equation

$$C_{p_2}(\text{app.})/\text{mole} = [161.44/x]\left[C_p/\text{g.} - \frac{C^0_{p1}\,(1 - x)}{18.016}\right] \tag{2}$$

Where 161.44 is the molecular weight of $ZnSO_4$, x is the weight fraction and C^0_{p1}, represents the molal heat capacity of pure water.

The values of C_{p_2} (app.), at both temperatures, were plotted against $1/A^{1/2}$ and were found to lie on two parallel, straight lines within the limit of experimental error. The line at 35° was 6.0 cal. deg.$^{-1}$ mole^{-1} above the one at 25°.

The equations for these lines give the partial molal heat capacities as follows

$$C_{p_2}\ (\text{apparent}) = \text{``}C^0_{p_2}\text{''} + \text{const.}/A^{1/2} \tag{3}$$

---

[7] Seidell, "Solubilities of Inorganic and Metal Organic Compounds," Vol. I, D. Van Nostrand Co., New York, N. Y., 1940, p. 1593.

[8] Harned and Owen, "Physical Chemistry of Electrolytic Solutions," A. C. S. Monograph No. 95, Reinhold Pub. Corp., New York, N. Y., 1943, p. 425.

[9] Harned, THIS JOURNAL, **59**, 360 (1937).

[10] Osborne, Stimson and Ginnings, *J. Research Natl. Bur. Standards*, **23**, 197 (1939).

[11] Rossini, *J. Research Natl. Bur. Standards*, **7**, 47 (1931).

$$\overline{C}_{p1} = C^0_{p1} - \text{const.}/2A^{3/2} \quad (4)$$

$$\overline{C}_{p2} = \text{``}\overline{C}^0_{p2}\text{''} + 3\ \text{const.}/2A^{1/2} \quad (5)$$

The following equations hold over the range $A = 15.6$ to $A = 72$. At 25°

$$C_{p2}(\text{apparent}) = -39.8 + 191/A^{1/2} \quad (6)$$

$$\overline{C}_{p2} = -39.8 + 3 \times 191/2A^{1/2} \quad (7)$$

$$\overline{C}_{p1} = 17.996 - 191/2A^{3/2} \quad (8)$$

at 35°

$$C_{p2}\ (\text{apparent}) = -33.8 + 191/A^{1/2} \quad (9)$$

$$\overline{C}_{p2} = -33.8 + 3 \times 191/2A^{1/2} \quad (10)$$

$$\overline{C}_{p2} = 17.991 - 191/2A^{3/2} \quad (11)$$

The values of "$C^0_{p_2}$" given above are purely empirical constants rather than the values at infinite dilution.

In Table IV, values of the heat capacity of $ZnSO_4$ solutions calculated from the above equations are compared with the measured values corrected to 25 and 35°. The equation

$$C_{p2}\ (\text{apparent}) = -218.7 + 0.6T + 191/A^{1/2} \quad (12)$$

satisfies values at both 25 and 35° over the range $A = 15.6$ to $A = 70$.

Giauque, Kunzler and Barieau[12] have extended the partial molal heat capacities of $ZnSO_4$ solution to infinite dilution by means of available cell measurements and data combined with the third law of thermodynamics.

TABLE IV

HEAT CAPACITY OF $ZnSO_4$ SOLUTIONS

	C_p, cal. deg.$^{-1}$ g.$^{-1}$			
A	25°, obsd.	25°, calcd.	35°, obsd.	35°, calcd.
15.6570	0.6544	0.6544	0.6658	0.6677
21.7229	.7105	.7093	.7213	.7199
29.7402	.7607	.7608	.7708	.7692
40.4008	.8066	.8066	.8126	.8131
55.0072	.8454	.8468	.8523	.8517
72.4615	.8774	.8772	.8786	.8810

The Heat of Solution of $ZnSO_4 \cdot 7H_2O$ in Water to Form a Saturated Solution.—By combining the heat of dilution data given in Table II, with the similar data of Lange, Monheim and Robinson[6] for solutions below 1 molal, and the heat of solution of $ZnSO_4 \cdot 7H_2O$ given by Barieau and Giauque,[2] one obtains the heat of solution of zinc sulfate heptahydrate in enough water to form a saturated solution.

$$(ZnSO_4 + 55.506H_2O)_{\text{soln.}} = (ZnSO_4 + 15.598H_2O)_{\text{satd. soln.}} + 39.908H_2O$$

$$\Delta H_{25^\circ} = 836 \text{ cal. mole}^{-1} \quad (13)$$

$$(ZnSO_4 + 543H_2O)_{\text{soln.}} = (ZnSO_4 + 55.506H_2O)_{\text{soln.}} + 487.494H_2O$$

$$\Delta H_{25^\circ} = 314 \text{ cal. mole}^{-1} \quad (14)$$

$$ZnSO_4 \cdot 7H_2O_{(s)} + 536H_2O = (ZnSO_4 + 543H_2O)_{\text{soln.}}$$

$$\Delta H_{25^\circ} = 4270 \text{ cal. mole}^{-1} \quad (15)$$

Adding equations 13, 14 and 15

$$ZnSO_4 \cdot 7H_2O_{(s)} + 8.598H_2O = (ZnSO_4 + 15.598H_2O)_{\text{sat. soln.}} \quad (16)$$

$$\Delta H_{25^\circ} = 5420 \text{ cal. mole}^{-1}$$

Thermodynamic Treatment of the Data on the Clark Cell.—The e. m. f. of the Clark cell represents the reaction

$$Zn + Hg_2SO_4 + 7H_2O\ (\text{satd. } ZnSO_4 \text{ soln.}) = ZnSO_4 \cdot 7H_2O(s) + 2Hg \quad (17)$$

$$\Delta F_{(17)} = -2F\mathbf{E}$$

The zinc is ordinarily used as an amalgam; however, Clayton and Vosburgh[13] have shown that there is no potential for the cell

$$Zn = Zn(\text{2-phase amalgam}) \quad (18)$$

Equation 17 may be simplified by considering the reaction

$$H_2O(l) = H_2O(\text{satd. } ZnSO_4 \text{ soln.}) \quad (19)$$

$$\Delta F_{(19)} = RT \ln a_1 \quad (20)$$

where a_1 represents the activity of the water in saturated zinc sulfate solution.

Equation 17 and 7 times Equation 19 may be added to give the equation

$$Zn + Hg_2SO_4 + 7H_2O(l) = ZnSO_4 \cdot 7H_2O(s) + 2Hg \quad (21)$$

Robinson and Jones[14] have obtained the activity of water from their measurements of its partial pressure over zinc sulfate solutions from 0.1 M to saturation at 25°.

In order to apply Equation 19 at the various temperatures, it is necessary to know the activity of water in zinc sulfate solutions over a range of temperature. The measurements of relative partial molal heat contents, and partial molal heat capacities, given above, were made in order to permit the above calculation to be made with high accuracy, by means of the thermodynamic equations

$$\frac{d\ \Delta F_{(19)}/T}{dT} = \frac{-\overline{L}_1}{T^2} \quad (22)$$

and

$$\frac{d\overline{L}_1}{dT} = \overline{C}_{p1} - C^0_{p1} = -\frac{191}{2A^{3/2}} \quad (23)$$

$$\frac{\Delta F_{(19),\ T}}{T} - \frac{\Delta F_{(19),\ 25^\circ}}{2981.6} = -\int_{298.16}^{T} \overline{L}_1/T^2\, dT \quad (24)$$

$\Delta F_{(19),\ 25^\circ}$ was calculated from Equation 19, using the activity of water in a solution of a concentration which corresponded to saturation at a lower temperature T.

The numerous determinations of the solubility of zinc sulfate are summarized by Seidell,[7] who gives full weight to the careful determinations of Cohen and Hetterschij,[15] over the range of $ZnSO_4 \cdot 7H_2O$. Also, we prefer to accept the results of one research in the present work; since, from the nature of the test, a series of solubility determina-

---

(12) Giauque, Kunzler and Barieau, to be published.

(13) Clayton and Vosburgh, THIS JOURNAL, **58**, 2093 (1936).

(14) Robinson and Jones, *ibid.*, **58**, 959 (1936). Robinson, *Trans. Proc. Roy. Soc. New Zealand*, **75**, 203 (1945), has reconsidered the activity of water over the KCl solutions which were used as a standard in the work of R. and J. The maximum change was 0.04%, with the average less than half this amount. Since we consider the changes to be within the limit of error, and since in any case, the change would not affect any result in the present research by more than one cal. mole^{-1}, we have used the results of R. and J., unaltered.

(15) Cohen and Hetterschij, *Z. physik. Chem.*, **115**, 440 (1925).

tions which were systematically high or systematically low would have little effect on the conclusion drawn.

The calculation of $\Delta F_{(19)}/T$ is outlined in Table V.

TABLE V

FREE ENERGY OF THE REACTION

$H_2O(l) = H_2O(ZnSO_4 \text{ satd. soln.})$

	Cohen and Heterschij[15]	This research		Robinson and Jones[14]	$\Delta F_{(19)}$,
t, °C.	A moles H_2O/mole $ZnSO_4$	$\bar{L}_{1(25°)}$, cal. mole^{-1}	$\bar{C}_{p1} - C_{p1}^0$ cal. deg. mole^{-1}	$\Delta F_{(19),\,25°}/T$ cal. deg.$^{-1}$	$t°/T$, calcd. mole^{-1}
0	21.536	− 43	−0.956	−0.1361	−0.1455
5	20.178	− 47.5	−1.054	− .1551	− .1639
10	18.966	− 60	−1.156	− .1761	− .1852
15	17.801	− 81	−1.272	− .2013	− .2098
20	16.657	−115	−1.405	− .2327	− .2391
25	15.598	−163	−1.550	− .2698	− .2698

The available data on the e. m. f. of the Clark cell were plotted in the form of the function

$$(\mathbf{E}_t - \mathbf{E}_{15°}) + 0.00127t \text{ against } t \qquad (25)$$

and a smooth curve was drawn through the observations.

The measurements of Callendar and Barnes[16] are by far the most self-consistent and they were given 100% weight in drawing the curve which passed either through or very near the observed points.

The $E_{15°}$ accepted as standard at the time of Callendar and Barnes' measurements was 1.4340. When the Weston cell was adopted as the standard for the international volt in 1908, it was found[17] that the e. m. f. of the Clark cell, as made in England, should be multiplied by 0.99870 to convert it to the adopted international volt. Accordingly the values of $\mathbf{E}_t = 1.4340 + (\mathbf{E}_t - \mathbf{E}_{15})$ obtained from Callendar and Barnes work have been multiplied by 0.99870.

One international volt equivalent has been taken as 23,063.2 cal., in conformity with the values of constants given by DuMond and Cohen,[18] in their report to the National Research Council.

The e. m. f. and free energy change in the Clark cell have been summarized in Table VI.

TABLE VI

FREE ENERGY, CAL. MOLE^{-1}, OF THE REACTION

$Zn + Hg_2SO_4 + 7H_2O(l) = ZnSO_4{\cdot}7H_2O(s) + 2Hg$

	Callendar and Barnes[16]			
t, °C.	E. m. f., inter volts	$\Delta F_{(17)}$	$7\Delta F_{(20)}$	$\Delta F_{(21)}$
0	1.44873	−66824.7	−278.2	−67102.9
5	1.44346	−66581.6	−319.1	−66900.7
10	1.43793	−66326.5	−367.0	−66693.5
15	1.43214	−66059.5	−425.0	−66484.5
20	1.42601	−65776.7	−490.7	−66267.4
25	1.41954	−65478.3	−563.1	−66041.4

In order to decide the question as to whether the $\int_0^T C_p \, d \ln T$ has given the correct entropy of $ZnSO_4{\cdot}7H_2O$, the following calculation is made.

$$Zn + Hg_2SO_4 + 7H_2O(l) = ZnSO_4{\cdot}7H_2O + 2Hg \qquad (21)$$

$$\Delta F_{(22)(T°K.)} = \Delta H_{298.16} + \int_{298.16}^{T} \Delta C_p dT - T(\Delta S_{298.16} + \int_{298.16}^{T} \Delta C_p d \ln T) \qquad (26)$$

Equation 26 may be used to calculate $\Delta H_{298.16°K.}$ from the free energy values at each of the temperatures considered above. If the quantity $\Delta S_{298.16°K.}$ has been correctly derived from the experimental data, the several values of $\Delta H_{298.16°K.}$ should agree. If $\Delta S_{298.16°K.}$ is incorrect, the calculated values of $\Delta H_{298.16°K.}$ will be incorrect, and they will change linearly with temperature.

The values of the entropies of all of the reactants and products, with references, have been given in the previous paper.[2] At 298.16°K. the values are as follows: Zn, $S = 9.95$; Hg_2SO_4, $S = 48.0$; $H_2O(l)$, $S = 16.73$; $ZnSO_4{\cdot}7H_2O$, $S = 92.91$; Hg, $S = 18.48$ cal. deg.$^{-1}$ mole^{-1}.

The following approximate formulas were used to represent the heat capacities in cal. mole^{-1} of the several substances over the temperature range considered.

$$Zn, C_p = 5.29 + 0.0026T \qquad (27)$$

$$Hg_2SO_4, C_p = 13.8 + 0.060T \qquad (28)$$

$$H_2O(l), C_p = 19.79 - 0.006T \text{ (0 to 25°)} \qquad (29)$$

$$= 18.00 \text{ (25 to 60°)}$$

$$ZnSO_4{\cdot}7H_2O, C_p = 16.81 + 0.248T \qquad (30)$$

$$Hg, C_p = 7.368 - 0.0023T \qquad (31)$$

$$\Delta C_{p(21)} = -127.334 + 0.2228T \qquad (32)$$

The calculation of $\Delta H_{298.16°.K}$ is summarized in Table VII. The intermediate values have been given to 0.1 calorie in order to preserve internal consistency in the calculation.

TABLE VII

$\Delta H_{298.16°K.}$ FOR THE REACTION $Zn + Hg_2SO_4 + 7H_2O = ZnSO_4{\cdot}7H_2O + 2Hg$ CALCULATED FROM DATA AT SEVERAL TEMPERATURES

cal. mole^{-1}

T, °K.	ΔF_T	$T\Delta S$	$\Delta H_{298.16} - \Delta H_T$	$\Delta H_{298.16}$
273.16	−67,102.9	−10,819.9	−1592.3	−79,515
278.16	−66,900.7	−11,350.3	−1262.7	−79,514
283.16	−66,693.5	−11,881.4	− 938.6	−79,514
288.16	−66,484.5	−12,416.2	− 620.1	−79,521
293.16	−66,267.4	−12,943.3	− 307.3	−79,518
298.16	−66,041.4	−13,473.9	0.0	−79,515
			Av.	−79,516

The agreement of the values of $\Delta H_{298.16}$ in the last column of Table VII is excellent and there is no evidence of a trend with the temperature of the data used. Had there been an entropy discrepancy of $R \ln 2 = 1.4$ cal. deg.$^{-1}$ mole^{-1} in the $\int_0^T C_p d \ln T$ for $ZnSO_4{\cdot}7H_2O$, corresponding to

---

[16] Callendar and Barnes, *Proc. Roy. Soc.* (*London*), **62**, 117 (1897).

[17] "Int. Critical Tables," Vol. I, p. 27.

[18] DuMond and Cohen, *Rev. Mod. Phys.*, **20**, 82 (1948).

false equilibrium with respect to two choices of position for one H_2O molecule per mole of $ZnSO_4\cdot 7H_2O$, the trend would have been 35 cal. mole^{-1} between 273.16 and 298.16°K.

The above result leads to the conclusion that $ZnSO_4\cdot 7H_2O$ attains a perfectly ordered crystalline state when it is cooled to very low temperatures.

Incidental to the determination of accurate values of ΔH and ΔS for the reaction described in Table VII a number of other quantities may be calculated.

The Heat of Reaction in the Clark Cell.—As is well known, cells involving solid phases of hydrated products or reactants must, for reasons of solubility, precipitate or dissolve more moles of hydrate than corresponds to the number of equivalents of electricity passed through the cell. This affects the heat of reaction. Appropriate equations for the Clark cell have been given by Cohen and Sinnige.[19]

For our present purposes it will be convenient to consider the Clark cell reaction in two parts

$$Zn + Hg_2SO_4 + 7H_2O = ZnSO_4\cdot 7H_2O + 2Hg \quad (21)$$
$$\Delta H_{298.16°\text{K.}} = -79{,}516 \text{ cal. mole}^{-1}$$

and

$$\frac{7}{A-7} ZnSO_4\cdot AH_2O_{(\text{satd. soln.})} = 7H_2O + \frac{7}{A-7} ZnSO_4\cdot 7H_2O \quad (33)$$

From Equation 16, the heat of solution of one mole of $ZnSO_4\cdot 7H_2O$ in enough water to form a saturated solution at 25° is 5420 cal. mole^{-1}. Since $A_{298.16} = 15.598$, the heat of Reaction 33 is

$$AH_{298.16°\text{K.}} = \frac{-5420 \times 7}{15.598\text{-}7} = -4413 \text{ cal.}$$

Adding Equations 21 and 33, gives the reaction in the Clark cell

$$Zn + Hg_2SO_4 + \frac{7}{A-7} ZnSO_4\cdot AH_2O_{(\text{satd. soln.})} = \frac{A}{A-7} ZnSO_4\cdot 7H_2O + 2Hg \quad (34)$$
$$\Delta H_{298.16°\text{K.}} = -83{,}929 \text{ cal. mole}^{-1}$$

Mees[20] has determined the heat of Reaction 34 at 18°. From the present results we may calculate as follows

$$\text{Reaction 21, } \Delta H_{291.16°\text{K.}} = -79{,}089 \text{ cal. mole}^{-1}$$

From our Equations 12, 29 and 30, and $A_{291.16°\text{K.}} = 17.052$

$$\text{Reaction 33, } \Delta H_{291.16°\text{K.}} = \frac{-4949 \times 7}{17.052 - 7} = -3446 \text{ cal.}$$

From which the heat of reaction in the Clark cell at 18° is

$$\Delta H_{291.16°\text{K.}} = -82{,}535 \text{ cal. mole}^{-1}$$

This reliable value may be compared to a result of $\Delta H_{18°} = -82{,}175$ cal. mole^{-1} obtained by Mees from calorimetric measurements. This becomes $\Delta H_{291.16°\text{K.}} = -82{,}241$ cal. mole^{-1} in terms of the defined calorie used in the present work. Mees used 1.0000 instead of 0.9998 cal. deg.$^{-1}$ mole^{-1} in calculating the water equivalent of his calorimeter and used 0.2389 instead of 0.23905 cal. joule^{-1}.

The Partial Pressure of Water over Saturated Solutions of $ZnSO_4\cdot 7H_2O$ and $ZnSO_4\cdot 6H_2O$.—The e. m. f. measurements of Callendar and Barnes[16] extend from 0 to nearly 50°. These data receive support from the accurate but somewhat less self consistent measurements of Cohen, Inouye and Euwen,[21] which extend to 55°.

These data combined with the results given above may be used to give very reliable values of the partial pressure of water over saturated solutions of $ZnSO_4$. The cell data have been extrapolated over a short range to 60.3°., which Barieau and Giauque[2] found to be the transition temperature at which the hexa- and monohydrates of zinc sulfate are in equilibrium with the saturated solution.

$$Zn + Hg_2SO_4 + 7H_2O(l) = ZnSO_4\cdot 7H_2O + 2Hg \quad (21)$$
$$Zn + Hg_2SO_4 + 7H_2O(l)_{\text{sat. soln.}(l)} = ZnSO_4\cdot 7H_2O + 2Hg \quad (17)$$

Subtracting Equation 17 from Equation 21 we can reverse and extend the previous calculation.

$$7H_2O(l) = 7H_2O(\text{sat. soln.}) \quad (19)$$
$$\Delta F = 7RT \ln a_1$$

The accepted values of $\Delta H = -79{,}516$ cal. mole^{-1} and $\Delta S = -45.19$ cal. deg.$^{-1}$ mole^{-1}, for Equation 21 at 298.16°K., together with the known heat capacities, permit the accurate calculation of the ΔF of this reaction at various temperatures, from 273.16°K. to the transition point 311.28°K., above which, the hexahydrate becomes the stable phase.

From the calorimetric results of Barieau and Giauque[2]

$$ZnSO_4\cdot 7H_2O = ZnSO_4\cdot 6H_2O + H_2O(l) \quad (35)$$
$$\Delta H_{298.16°\text{K.}} = 3452 \text{ cal. mole}^{-1}$$

and

$$ZnSO_4\cdot 6H_2O,\ C_p = 10.66 + 0.248T \quad (36)$$

and combining Equations 21 and 35

$$Zn + Hg_2SO_4 + 6H_2O = ZnSO_4\cdot 6H_2O + 2Hg \quad (37)$$
$$\Delta H_{298.16} = -76{,}064;\ \Delta S_{298.16} = -34.47$$

Above 311.28°K. the e. m. f. of the Clark cell corresponds to the reaction

$$Zn + Hg_2SO_4 + 6H_2O(\text{satd. soln.}) = ZnSO_4\cdot 6H_2O + 2Hg \quad (38)$$

Subtracting Equation 38 from Equation 37

$$6H_2O(l) = 6H_2O(\text{satd. soln.}) \quad (39)$$
$$\Delta F = 6RT \ln a_1$$

The data adopted have been summarized in Table VIII. Since the cell has been studied both supersaturated and supercooled, with respect to the hexa- and heptahydrates, values for each have

---

(19) Cohen and Sinnige, *Z. physik. Chem.*, **67**, 513 (1909).

(20) Mees, Thesis, Univ. of Utrecht, 1916.

(21) Cohen, Inouye and Euwen, *Z. physik. Chem.*, **75**, 1 (1910).

been given at 35 and 40°. The cell values cannot be represented satisfactorily by means of a simple equation.

TABLE VIII

THE VAPOR PRESSURE OF WATER OVER SATURATED SOLUTIONS OF ZINC SULFATE

T, °K.	E. m. f. Clark cell, int. volts	$-\Delta F$, Clark cell, cal. mole^{-1}	$-\Delta F_{(33)}$, cal. mole^{-1}	a_{H_2O}	P_{H_2O} mm., sat. soln.
$ZnSO_4 \cdot 7H_2O$					
273.16	1.44873	66824.7	67103.8	0.9292	4.26
278.16	1.44346	66581.6	66903.0	.9203	6.02
283.16	1.43793	66326.5	66696.0	.9105	8.38
288.16	1.43214	66059.5	66479.7	.9005	11.51
291.16	1.42850	65891.6	66357.3	.8914	13.80
293.16	1.42601	65776.7	66265.4	.8871	15.55
298.16	1.41954	65478.3	66042.1	.8729	20.73
303.16	1.41262	65159.1	65813.6	.8563	27.24
308.16	1.40534	64823.3	65580.1	.8382	35.34
311.28	1.40061	64605.1	65438.8	.8249	41.25
313.16	1.39852	64463.0	65341.8	.8173	45.21
$ZnSO_4 \cdot 6H_2O$			$-\Delta F_{(44)}$		
308.16	1.40399	64761.0	65432.9	.8329	35.12
311.28	1.40061	64605.1	65319.7	.8249	41.25
313.16	1.39753	64508.7	65251.3	.8197	45.34
318.16	1.39294	64251.3	65066.3	.8067	57.98
323.16	1.38722	63987.5	65878.1	.7937	73.43
328.16	1.38141	63719.5	65686.8	.7810	92.20
333.16	1.37553	63448.2	64492.4	.7689	114.9
333.46	1.37518	63432.1	64481.0	.7681	116.4
$ZnSO_4 \cdot H_2O$					

The partial pressures of water in the last column of Table VIII were based on the vapor pressures of water given by Osborne, Stimson and Ginnings.[22] The calculated values of vapor pressure should be quite accurate since any error in free energy is divided by 7 in the heptahydrate range and by 6 in the case of the hexahydrate. The values at 311.28°K.[2] and 333.46°K.[2] are of special interest since they represent transition pressures

$$ZnSO_4 \cdot 7H_2O = ZnSO_4 \cdot 6H_2O + H_2O(g) \quad (P = 41.25 \text{ mm.}) \qquad (40)$$

$$\Delta F_{311.28°K.} = 0$$

$$ZnSO_4 \cdot 6H_2O = ZnSO_4 \cdot H_2O + 5H_2O(g) \quad (P = 116.4 \text{ mm.}) \qquad (41)$$

$$\Delta F_{333.46°K.} = 0$$

The free energy corresponding to Equation 35 may be expressed as a function of temperature by means of available data

$$ZnSO_4 \cdot 7H_2O = ZnSO_4 \cdot 6H_2O + H_2O(l) \qquad (35)$$

$$\Delta H_{298.16} = 3452 \text{ cal. mole}^{-1}$$

$$H_2O(l) = H_2O(g)$$

$$\Delta H_{298.16} = 10{,}514 \text{ cal. mole}^{-1\ 10} \qquad (42)$$

Adding Equations 35 and 42

$$ZnSO_4 \cdot 7H_2O = ZnSO_4 \cdot 6H_2O + H_2O \qquad (43)$$

$$\Delta H_{298.16} = 13{,}966 \text{ cal. mole}^{-1}$$

The heat capacity of $H_2O(g)$ may be taken as 8.03 cal. deg.$^{-1}$ mole^{-1} from the work of Gordon[23] based on spectroscopic data and corrected for rotational stretching by Wilson.[24] The above value may be considered as constant over the temperature range of interest. Combining this value with Equations 30 and 36, $\Delta C_p = 1.88$ cal. deg.$^{-1}$ mole^{-1} for Equation 43. Thus, the heat of reaction for Equation 43 may be written

$$\Delta H = 13{,}405 + 1.88T \qquad (44)$$

Equation 41 may be combined with the dissociation pressure at 311.28° K. to give the free energy of Equation 40

$$\Delta F_{(40)} = 13{,}405 - 1.88T \ln T - 26.48135T \qquad (45)$$
$$= -RT \ln P_{H_2O(\text{atmos.})}$$

At 298.16° K. this equation gives the value $P_{H_2O} = 15.27$ mm. which may be compared with the average value 15.35 mm., obtained from the average of several observers listed by Barieau and Giauque[2] in their Table V. It may be pointed out that with the assistance of the thermodynamic Equations 22 and 23, and the activity of water at 25° as measured by Robinson and Jones,[14] the partial pressure of water may be accurately calculated as a function of composition and temperature at zinc sulfate concentrations in the range $A = 15.6$ to $A = 72$.

Summary

The partial molal heat contents and heat capacities for aqueous zinc sulfate have been determined over the range 25 to 35°.

The Clark cell has been treated thermodynamically and the partial pressure of water over saturated $ZnSO_4$ solutions has been determined.

Various calorimetric and cell data have been combined to show that $ZnSO_4 \cdot 7H_2O$ attains perfect order at 0°K.

BERKELEY, CALIFORNIA RECEIVED APRIL 20, 1949

---

[22] Osborne, Stimson and Ginnings, *J. Research Natl. Bur. Standards*, **23**, 261 (1939).

[23] Gordon, *J. Chem. Phys.*, **2**, 65 (1934).

[24] Wilson, *ibid.*, **4**, 526 (1936).