tion by anodic polarography. When several metals are present in a dilute amalgam the quantitative estimation of the individual metals by anodic polarography is less satisfactory than for a single metal.

PRINCETON, N. J. RECEIVED APRIL 18, 1950

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

$ZnSO_4 \cdot 7H_2O$. $ZnSO_4 \cdot 6H_2O$. Heat Capacities, Entropies and Crystal Perfection at Low Temperatures. Heats of Solution and Transition

BY R. E. BARIEAU AND W. F. GIAUQUE

The work reported in this paper is related to a study of magnetic properties of compounds of the elements of the first transition period, particularly the heptahydrates of ferrous, cobaltous and nickel sulfates. The splitting of the energy levels of these paramagnetic ions is attributed to the electric fields of the water molecules which surround the ion. It is customary to assume that the water molecules are arranged in a definite crystalline pattern about the ion so that the arrangement can be considered to have some simple form of symmetry with respect to the electric fields due to the water molecules. While this is undoubtedly true in most cases there may be numerous exceptions. There are few data relating to this point.

It has been shown experimentally by Giauque and Stout[1] that the hydrogen bond structure of ice is completely random with respect to the four tetrahedral bond positions around each oxygen, as suggested by Bernal and Fowler,[2] and by Pauling,[3] who predicted the entropy discrepancy corresponding to the assumed disorder.

Long and Kemp[4] have shown that the deuterium bond disorder in deuterium oxide ice is the same as that which occurs in ordinary ice.

Pitzer and Coulter[5] have found a discrepancy in the entropy of $Na_2SO_4 \cdot 10H_2O$ which is probably due to disordered hydrogen bonds. In any case, the entropy discrepancy proves that the crystal is disordered in some respect.

The electric fields of a central ion about which the water molecules are arranged are certainly a powerful influence in producing perfect order but this alone may well be insufficient to prevent one or more of the water molecules from forming hydrogen bonds in more than one way.

$ZnSO_4 \cdot 7H_2O$ was selected for investigation because this substance, being diamagnetic, would avoid the additional complications which can arise in paramagnetic systems. Otherwise, this substance is rather similar to the other divalent heptahydrated sulfates of the first transition series.

Quite aside from the desirability of knowing that a crystal is perfect before attempting to explain various specific characteristics, such as magnetic properties, the problem is outstanding in the application of the third law of thermodynamics. Since the work on ice a considerable amount of work has been started in this Laboratory on related problems. Forsythe and Giauque[6] have presented substantial evidence which indicates that nitric acid and its mono- and trihydrates attain zero entropy and thus crystal perfection at the absolute zero. Other work was interrupted by the war and has only recently been resumed.

The present work, which includes the heat capacities of $ZnSO_4 \cdot 7H_2O$ and $ZnSO_4 \cdot 6H_2O$, to low temperatures, and their heats of solution, was intended as an investigation of both the hepta- and hexahydrates of zinc sulfate; however this latter substance underwent a thermodynamically irreversible transformation at low temperatures. This arrangement in the solid was so slow that it is questionable whether the data obtained on the hexahydrate can be used as evidence in the original objective.

We may say at once that $ZnSO_4 \cdot 7H_2O$ has been found to obtain an ordered arrangement at low temperatures and that the measurements on the hexahydrate, such as they are, give some indication that this substance may retain disorder.

Preparation of $ZnSO_4 \cdot 7H_2O$ and $ZnSO_4 \cdot 6H_2O$.—The sample of zinc sulfate heptahydrate was prepared by bubbling purified dry air through a saturated solution of Baker C. P. zinc sulfate heptahydrate at room temperature.

After a considerable amount of solid had precipitated, the solution, in a 2-liter flask, was cooled to about 0° in the presence of the solid, and then the crystals of $ZnSO_4 \cdot 7H_2O$ were filtered off. The above method was followed because Bury[7] has shown that it is possible to prepare a metastable monoclinic form of $ZnSO_4 \cdot 7H_2O$ below 25°. Bury[7] found that the metastable monoclinic form and the hexahydrate are in equilibrium with the saturated solution at 24.8°, and that the stable rhombic $ZnSO_4 \cdot 7H_2O$ and the hexahydrate are in equilibrium with the saturated solution between 38 and 39°.

Proof that the above method of preparation gave the stable rhombic form in the present work is furnished by the fact that during the heat capacity measurements no isothermal absorption of heat was observed at 25°, while there was such an absorption of heat between 38 and 39°. The temperature of the transition was determined as

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[1] Giauque and Stout, THIS JOURNAL, **58**, 1144 (1936).

[2] Bernal and Fowler, *J. Chem. Phys.*, **1**, 515 (1933).

[3] Pauling, THIS JOURNAL, **57**, 2680 (1935).

[4] Long and Kemp, *ibid.*, **58**, 1829 (1936).

[5] Pitzer and Coulter, *ibid.*, **60**, 1310 (1938).

[6] Forsythe and Giauque, *ibid.*, **64**, 48, 3069 (1942); **65**, 2379 (1943).

[7] Bury, *J. Chem. Soc.*, **125**, 2538 (1924).

38.12° during the present research. The samples of the heptahydrate used in the heat of solution measurements were part of the same preparation used for the low temperature heat capacity measurements.

Zinc sulfate hexahydrate was prepared by bubbling purified dry air through a saturated solution, kept at a temperature of about 50° by means of a thermostat, for two days. Near the end of the preparation the thermostat cooled to a temperature below 39° for an hour or so due to failure of the controls. When this was discovered the bath was raised again to 50°. Six hours later the crystals were removed by filtration. Analysis indicated that the sample was approximately 60 mole per cent. heptahydrate. On the possibly false assumption that this was due to incomplete drainage, the crystals were transferred to a beaker and reheated by means of a water-bath to 50°. They were then placed in a water jacketed Buchner funnel and air was passed over them until they appeared dry. During this procedure the water jacket was kept in the range 30-60°. Portions of the same sample were used for both the heat capacity and heat of solution measurements.

An electrometric titration showed that neither the hexa- nor heptahydrate contained more than the order one-hundreth of one per cent. of basic material computed as $Zn(OH)_2$.

Previous experience in attempting to prepare hydrates with exactly the right composition has shown this to be unusually difficult; thus it had been decided to prepare a sample of heptahydrate which was slightly deficient in water content and thus would contain some hexahydrate. A sample of hexahydrate was desired that contained a small excess of water and thus some heptahydrate. Measurements on each substance could then be corrected for the presence of a small amount of the other. For this reason the fact that the sample cooled to 30° for a brief period during the preparation was not considered important at the time. The above preparation of the hexahydrate was completed on March 22, 1940. Later in that year, a paper by Copeland and Short[8] appeared, which showed that the hexahydrate is unstable with respect to the reaction

$$6ZnSO_4 \cdot 6H_2O = 5ZnSO_4 \cdot 7H_2O + ZnSO_4 \cdot H_2O \quad (1)$$

below 21.5°, the transition temperature. It seems probable that this reaction is related to the irreversible behavior of the hexahydrate which will be described below. A re-examination of $ZnSO_4.6H_2O$ is now being made by Mr. C. H. Chu in this Laboratory.

Apparatus.—The low temperature heat capacity measurements were made in a calorimeter described by Giauque and Archibald.[9] The heat capacity of the empty calorimeter was redetermined.

The gold resistance thermometer-heater was calibrated by means of a standard copper-constantan thermocouple with the laboratory designation W-26. This was one of eight thermocouples calibrated by Giauque and Egan.[10] The calibration of the resistance thermometer was done concurrently with the heat capacity measurements. Before any measurements of heat capacity were made, the thermocouple was found to be in agreement with its original calibration when it was checked against the vapor pressure of solid and liquid hydrogen, and against the boiling point of oxygen. These comparisons were carried out while the thermocouple was in the assembled apparatus. The use of liquid oxygen as a standard is undesirable in such cases if it comes in contact with organic insulating material on wire. Liquid nitrogen is now used for this purpose in this Laboratory unless the calorimeter happens to be of the type in which oxygen can be condensed to a liquid inside the calorimeter.

At the conclusion of the work the thermocouple was again checked against the boiling and triple points of hydrogen. It is of interest to note that Lyon and Giauque[11] compared this same thermocouple with the triple (13.92°) and boiling (20.36°) points of hydrogen and the transition (35.62°), triple (63.15°) and boiling (77.34°) points of nitrogen in 1948, some 8 years later, and it was still in agreement with the original calibration within the 0.05° limit of error.

The heat capacity calculations were made in the manner described by Giauque, Wiebe and Johnston.[12] A few of the measurements on zinc sulfate hexahydrate required special treatment, by a method to be described later, because of the exceedingly low rate of approach to equilibrium.

The heat of solution measurements were made in an apparatus described by Giauque and Archibald.[9] To eliminate distillation which could have occurred if the solution had been cooled by lowering the external temperature, a glass bulb was placed in the calorimeter in which liquid water could be added and then pumped out at reduced pressure. This served to cool the apparatus in order that the heat capacity could be determined.

With the apparatus so constructed the heat of solution of KCl was determined. The test results are given in Table I.

TABLE I

HEAT OF SOLUTION OF KCl, CAL. MOLE^{-1}

Sample	Final molality	ΔH
I	0.1811	4194
II	.1811	4193
III	.1811	4206
	Av.	4198 ± 6

From the work of Lange and Monheim[13] the heat of solution to form a solution of this final concentration is 4199 cal. mole^{-1}.

Method of Analysis.—All samples were analyzed by dehydration. The method was to heat the sample for a day or two at 40-60° and then for an approximately equal time at 100°. Finally the temperature was increased to 310-320° and held until there was no further loss of weight with time. The weight became constant in about a week. One sample was held at about 310-320° for 130 days without changing in weight appreciably from the value obtained in 8 days. After the analyses had been made in this way additional tests were performed at higher temperature, to check on the complete dehydration of the samples. It was found that heating residues, prepared as above, to 500° caused them to lose 0.07% more weight. The several analyses were corrected by this amount.

A method of analysis based on the precipitation of zinc diethyldithiocarbamate was tried by adding sodium diethyldithiocarbamate to zinc sulfate solution. The method was tested by converting known amounts of pure zinc metal to the sulfate and it was found that the results averaged 0.3% high. The results had a spread of about 0.2% so the dehydration method was used because of its greater accuracy.

The interpretation of the over-all composition given by analysis proved to be much more involved than expected. The sample of heptahydrate had deliberately been prepared so as to have a small amount of hexahydrate on the surface of the crystals to avoid the possible presence of excess water. Excess water gives rise to a considerable absorption of heat at the ice-hydrate eutectic temperature. However, despite an over-all composition which was shown by analysis to be $ZnSO_4 \cdot 6.949H_2O$, there was a rise in heat capacity near the ice-heptahydrate eutectic temperature, −6.55°.[14] One possible explanation was that during the cooling of the calorimeter, which contained helium gas to improve thermal conductivity and reduce diffusion rate, some water vapor had distilled to the wall

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[8] Copeland and Short, THIS JOURNAL, **62**, 3285 (1940).

[9] Giauque and Archibald, *ibid.*, **59**, 561 (1937).

[10] Giauque and Egan, *J. Chem. Phys.*, **5**, 45 (1937).

[11] Lyon and Giauque, THIS JOURNAL, **71**, 1647 (1949).

[12] (a) Giauque and Wiebe, *ibid.*, **50**, 101 (1928); (b) Giauque and Johnston, *ibid.*, **51**, 2300 (1929).

[13] Lange and Monheim, *Z. Elektrochem.*, **35**, 29 (1929).

[14] "International Critical Tables," Vol. IV, McGraw-Hill Book Co., Inc., New York, N. Y., 1928, p. 255.

of the calorimeter where it remained as ice. However, it is possible to calculate from the rate of cooling and the thermal conductivity of the calorimeter plus the sample, determined during the heat capacity measurements, that when the calorimeter was cooled from room temperature to below the ice point, the temperature of the outside of the calorimeter was 4° below the average temperature of the calorimeter. It is possible to show that this temperature difference is not large enough to cause distillation of water from the crystals to the wall of the calorimeter.

It seems necessary to conclude that when the $ZnSO_4 \cdot 7H_2O$ crystals were formed in contact with the saturated solution, a small amount of solution was entrapped within the crystals. Subsequent drying caused the formation of some hexahydrate on the outside surface of the crystals without the loss of water from the entrapped solution. Measurements of heat capacity near an ice–hydrate eutectic are a sensitive test of solution inclusion. Our correction problem would have been simpler had the composition been selected as one with a slight excess of water although, had we done so in the present case, we would have been unaware of the above crystal imperfection and this important way of evaluating it.

During the heat capacity measurements to be given later it was found that 15.1 cal. in excess of the heat capacity was absorbed in the eutectic region by the amount of "heptahydrate" in the calorimeter. The reaction which occurred was

$$\frac{1}{A-7}ZnSO_4 \cdot 7H_2O + H_2O(s) = \frac{1}{A-7}ZnSO_4 \cdot AH_2O(\text{satd. soln.}) \quad (2)$$

A is the number of moles of water per mole of $ZnSO_4$ in the saturated solution. From the work of Cohen and Hetterschij[15] A is estimated to be 24 at −6.55°.

The heat of the above reaction is principally the heat of fusion of ice which was taken as 1377 cal. mole^{-1} at −6.55°; however, the heat of the reaction

$$\frac{1}{A-7}ZnSO_4 \cdot 7H_2O + H_2O(l) = \frac{1}{A-7}ZnSO_4 \cdot AH_2O(\text{satd. soln.}) \quad (3)$$

was estimated approximately by means of heat of solution and heat capacity data to be given later as $\Delta H = 259$ cal. mole^{-1} of water.

Thus the total heat of Reaction 2 is 1636 cal. mole^{-1} of ice.

The calorimeter contained 167.363 g. of "heptahydrate." The weight was corrected to a vacuum basis. The analysis showed that this amount contained 0.58388 mole of $ZnSO_4$. Thus there were 15.1/1636 × 0.58388 = 0.016 mole of ice per mole of zinc sulfate.

The over-all analysis showed that there were 6.949 moles of H_2O per mole of $ZnSO_4$, thus there must have been 6.933 moles of H_2O actually combined with $ZnSO_4$ below the eutectic temperature. The "heptahydrate" composition was 0.933 mole $ZnSO_4 \cdot 7H_2O$; 0.067 mole $ZnSO_4 \cdot 6H_2O$; 0.016 mole $H_2O(s)$.

There was no evidence of the similar inclusion of solution in the "hexahydrate" and none would be expected since even if small inclusions had occurred they would in all probability combine with adjacent hexahydrate to form $ZnSO_4 \cdot 7H_2O$ when the substance was cooled below 38.12°.

The sample of "hexahydrate" placed in the calorimeter weighed 171.343 g. *in vacuo* and the analysis showed the composition to be 0.979 mole $ZnSO_4 \cdot 6H_2O$; 0.021 mole $ZnSO_4 \cdot 7H_2O$. The calorimeter contained 0.63479 mole of $ZnSO_4$.

The Heat Capacities of Zinc Sulfate Hepta- and Hexahydrates.—In calculating the heat capacity 1 defined calorie was taken equal to 4.1833 international joules and 0° = 273.16°K. The data of Giauque and Stout[1] were used to subtract the heat capacity of 0.016 mole of ice per mole of "heptahydrate" and a small correction was also applied for the heat capacity of the helium which was used to ensure good thermal equilibrium.

The observations above the eutectic point are corrected for the heat of solution of $ZnSO_4 \cdot 7H_2O$ in the 0.016 mole of water present by inclusion. The solubility measurements of Cohen and Hetterschij[15] together with heat of solution data were used for this purpose.

The results are given in Table II.

TABLE II

HEAT CAPACITY OF $ZnSO_4 \cdot 6.933H_2O$ CAL. DEG.$^{-1}$ MOLE^{-1}

Average mol. weight, 286.34 g.; 0.58388 mole in the calorimeter; 0°C. = 273.16°K.

T, °K.	ΔT approx.	C_p	T, °K.	ΔT(approx.)	C_p
14.06	1.11	1.04	144.17	6.75	50.21
15.66	1.99	1.45	151.02	6.95	52.19
17.75	2.25	2.04	158.36	7.74	54.33
20.26	2.34	2.90	166.29	7.65	56.58
22.64	2.18	3.83	173.63	7.15	58.63
25.46	3.43	5.01	181.17	7.49	60.68
28.84	3.13	6.52	188.44	7.04	62.72
31.96	2.96	7.97	195.41	6.57	64.57
35.20	3.51	9.55	202.59	7.73	66.80[a]
39.43	4.77	11.64	210.34	7.31	68.58
43.73	3.80	13.66	218.16	8.29	70.67
47.60	3.95	15.52	226.39	7.82	72.77
52.16	5.03	17.72	234.00	7.42	74.74
56.85	4.20	19.89	241.52	7.06	76.63
61.17	4.38	21.73	248.43	6.75	78.37
65.67	4.59	23.64	255.30	6.51	80.09
70.36	4.82	25.55	261.68	6.26	81.63
75.44	5.31	27.55	267.97	6.31	83.12[b]
80.86	5.55	29.62	274.87	6.87	84.77[b]
86.59	5.92	31.70	281.86	6.58	86.69
92.61	6.12	33.86	288.58	6.33	88.33
98.80	6.16	35.97	295.21	6.09	90.07
104.93	6.13	38.01	301.49	5.89	91.52
111.10	6.13	40.04	297.27	5.80	90.75
117.48	6.65	42.03	297.72	4.94	90.52
124.24	6.68	44.18	303.40	5.98	91.92
130.86	6.56	46.18	308.01	4.64	93.73
137.48	6.67	48.19			

[a] High point because insulating vacuum was partially lost during the measurement. [b] Values used as base of curve for estimating heat absorbed in eutectic region due to solution inclusion.

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(15) Cohen and Hetterschij, *Z. physik. Chem.*, **116**, 440 (1925).

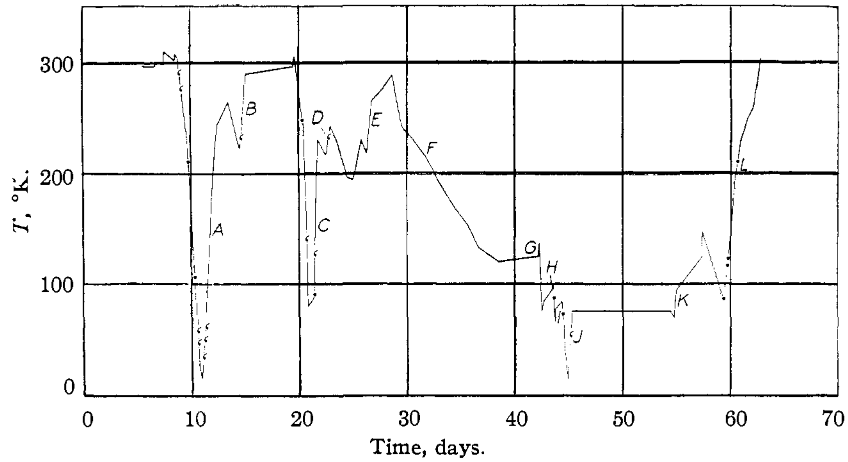

Fig. 1.—Thermal history of zinc sulfate hexahydrate sample used in the heat capacity measurements. Zero on the time axis corresponds to 12:01 A.M. March 22, 1940.

Some of the heat capacity measurements on zinc sulfate hexahydrate are shown in Fig. 3. Because of the very unusual experimental results we have given the thermal history of the sample in Fig. 1. The letters in the figure refer to the heat capacity series. When a temperature of 240°K. was reached at the end of series A, the drift measurements became very abnormal. At the time we thought this might be due to the sublimation of a small amount of adsorbed water which had possibly condensed on the wall of the calorimeter. For this reason the measurements were stopped and the sample allowed to warm to 265°K. The sample was then cooled to 220°K. and series B was measured. Series A and Series B did not agree with one another; so the sample was then cooled to liquid air temperature. One heat capacity was measured at this temperature. Following this the sample was heated to 175°K. and series C was taken. Series D and E were taken to find out if the heat capacity determinations near 240°K. were reversible. It was found that they were not. It was then decided to cool the sample very slowly, hoping that the time spent at each temperature would be long enough for the sample to come to equilibrium. Series F was taken while the sample was cooling. The rate of energy input during these determinations was usually less than the rate of energy loss by radiation. The final temperature was thus less than the initial temperature.

Series G was next measured, and then the calorimeter was cooled to 75°K. A heat capacity determination was started, but at the end of the measurement the sample warmed up and continued to warm up for four hours, even though the environment was colder than the calorimeter. Another determination was then attempted, and the sample again warmed up at the end of the experiment. The next day the sample was at 95°K. and series H was measured. At this time there was no evidence of irreversible effects taking place in the calorimeter, and when the sample was again cooled to 65°K. and series I measured, there was no evidence of irreversibility. It was then decided to cool the sample to liquid hydrogen temperatures again. When the sample had cooled to 48°K., the helium was pumped out of the insulating vacuum space, and the rate of cooling of the sample was observed. No evidence of irreversibility was found. The vacuum was then broken and the sample cooled to liquid hydrogen temperatures. Following this, heat capacity Series J was measured, ending at 75°K. It was impossible at this time to continue the measurements. The sample was kept at liquid air temperature until the next series of measurements. Series K was measured to ensure that the heat capacity did not change with time while the sample was standing at liquid air temperature. A few days later Series L was started. These measurements, extending from 85 to 305°K., were made continuously.

From 230 to 270°K. the approach to thermal equilibrium was very slow. For most of the determinations between these temperatures, observations were taken for at least an hour after energy input, and the sample was still not in thermal equilibrium. Because of this it was necessary to calculate these determinations in a special manner. The drift of the calorimeter in degrees per minute was calculated at several intervals and then corrected for that part of the drift that was due to heat leak. The logarithm of the resulting quantity was plotted against the time, and it was found that a straight line represented the points in a satisfactory manner. The resulting curve was used to extrapolate the temperatures to infinite time from the last observation. The initial temperature of the following determination was corrected in a similar manner. This correction never amounted to more than 0.2%. A typical curve is shown in Fig. 2.

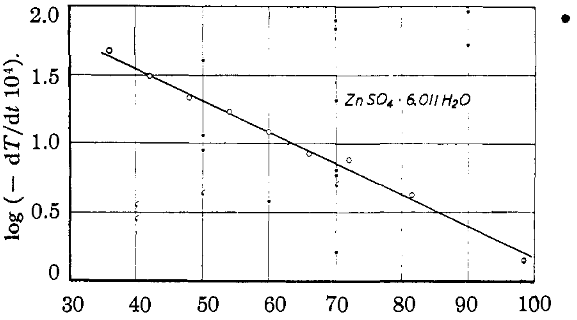

Fig. 2.—Approach to thermal equilibrium of zinc sulfate hexahydrate. The logarithm of the drift, corrected for heat leak, is plotted against the time; $T = 243$°K.

The slope of the curve was practically independent of temperature. Series A, B, J, K and L are shown in Fig. 3. The points of Series L illustrate the effect of the irreversibility. The detailed data are not included.

In order to obtain the heat capacity of pure $ZnSO_4 \cdot 7H_2O$ it is necessary to correct for the 6.7 mole % of $ZnSO_4 \cdot 6H_2O$ which it contained. Since the "heptahydrate" showed no evidence of a maximum near 250°K. nor of the hysteresis which complicated the measurements with the "hexahydrate," the correction was based on a curve for $ZnSO_4 \cdot 6.021\ H_2O$ which passed smoothly through the points below the maximum as shown in Fig. 1.

The fact that the 6.7 mole % hexahydrate in the "heptahydrate" showed no abnormality indicates that it should be possible to measure its heat capacity without encountering the disturbances which interfered with the present measurements.

The heat capacity of $ZnSO_4 \cdot 7H_2O$ is given in Table III. The values have been read from a smooth curve through the data and we believe that the results are reliable since any uncertainty was minimized by the moderate size of the

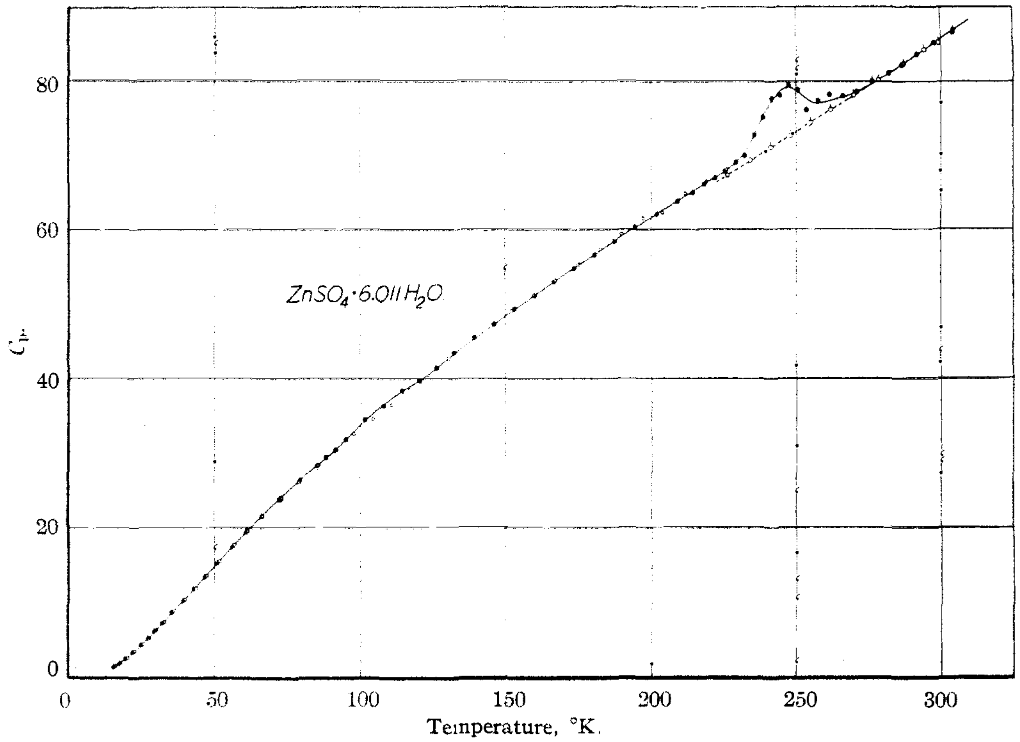

Fig. 3.—Heat capacity of $ZnSO_4 \cdot 6.011\ H_2O$ in calories per degree per mole: O, Series A; ȯ, Series B; ♁, Series J; ⚲, Series K; ●, Series L.

correction. However, the similar results, also given for $ZnSO_4 \cdot 6H_2O$ in Table III, must be considered open to question since the nature of the transformation which occurred at low temperatures is not definitely known.

TABLE III

HEAT CAPACITIES OF $ZnSO_4 \cdot 7H_2O$ AND $ZnSO_4 \cdot 6H_2O$, CAL. DEG.$^{-1}$ MOLE^{-1}

Smoothed values calculated from observations; mol. wts. 287.55 and 269.54; 0°C. = 273.16°K.

T, °K.	C_p $ZnSO_4 \cdot 7H_2O$	C_p $ZnSO_4 \cdot 6H_2O$	T, °K.	C_p $ZnSO_4 \cdot 7H_2O$	C_p $ZnSO_4 \cdot 6H_2O$
15	1.31	1.15	150	52.14	48.47
20	2.83	2.43	160	55.04	51.31
25	4.85	4.19	170	57.87	54.06
30	7.11	6.16	180	60.65	56.73
35	9.53	8.32	190	63.39	59.32
40	12.01	10.49	200	66.11	61.84
45	14.43	12.65	210	68.80	64.28
50	16.81	14.80	220	71.46	66.63
60	21.39	18.96	230	74.09	68.91
70	25.60	22.81	240	76.65	71.15
80	29.50	26.44	250	79.16	73.36
90	33.16	29.88	260	81.63	75.59
100	36.62	33.15	270	84.08	77.95
110	39.92	36.32	280	86.56	80.41
120	43.10	39.44	290	89.08	82.93
130	46.18	42.52	300	91.64	85.49
140	49.19	45.54	310	94.24	88.09

The Irreversible Process in $ZnSO_4 \cdot 6H_2O$.—The irreversible process which occurred in $ZnSO_4 \cdot 6H_2O$ caused a maximum increase in heat capacity near 250°K. The rise in the curve was spread principally over the range 230 to 270°K. However other erratic disturbances occurred as low as 100°K. and the thermal history influenced the heat capacity curve to some extent at all temperatures down to the temperature of liquid hydrogen.

It has been suggested above that the disturbance is connected with the fact that $ZnSO_4 \cdot 6H_2O$ is unstable with respect to the phases $ZnSO_4 \cdot 7H_2O$ and $ZnSO_4 \cdot H_2O$ as shown by Copeland and Short.[8]

$$6ZnSO_4 \cdot 6H_2O = ZnSO_4 \cdot H_2O + 5ZnSO_4 \cdot 7H_2O \quad (1)$$

$\Delta F = 0$ at 21.5° and the heat of reaction is given by Bichowsky and Rossini[16] as $\Delta H = -1000$ cal. (approx.) per mole of $ZnSO_4 \cdot 6H_2O$. Since ΔC_p of Reaction 1 should be rather small we may take it as zero and estimate that ΔF would be of the order of -100 to -200 cal. mole^{-1} of hexahydrate at 250°K.

Consider the mechanism required to form a small region of monohydrate of the order of 10 molecular diameters on a side. About 5000 molecules of water would have to migrate out of this region and find their way into regions of heptahydrate where they would form 5000 molecules of this material. Phase regions of even this magnitude are unlikely but even these would not have the thermodynamic properties

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(16) Bichowsky and Rossini, "Thermochemistry of Chemical Substances," Reinhold Publ. Corp., New York, N. Y., 1936.

of the bulk material. It would obviously be highly improbable that such large amounts of water could be moved around in the solid state as would be required to make phase regions which would be more than colloidal in size. As is well known, surface energy can increase the free energy by a considerable amount as, for example, when small particle size increases solubility or vapor pressure by as much as a factor of two.

It is suggested that the irreversible disturbance in $ZnSO_4·6H_2O$ at low temperatures is related to the above effect. The free energy change is so small that surface energy effects should be able to reverse its sign and make such microscopic phase regions transform back to the parent substance at temperatures well below the normal transition temperature. It is noteworthy that the substance gave no evidence of a heat of transition when it was heated through the normal transition temperature, 21.5°, during heat capacity observations.

It might be expected that if the substance were kept just below 21.5° that the transition could take place slowly after crystal nuclei of the other phases were present. An examination of the complete thermal history, shown in Fig. 1, shows that the substance was never kept just below the transition point for very long. At temperatures above 21.5° the hexahydrate is stable and at low temperatures the rate of such a process should be extremely slow.

In attempting to visualize such adjacent microscopic regions of mono- and heptahydrate it is a little difficult to decide whether one should not consider the practicable limit of such a process to be a form of solution.

The only basis on which one can attempt to assign the heat capacities obtained in this research as a property of $ZnSO_4·6H_2O$ lies in the idea that the transformation is so complex that it has occurred to a relatively minor extent. In this connection the amount of extra energy under the maximum in the heat capacity curve is not encouraging since it amounts to the order of 200 cal. mole^{-1} and a small particle size should decrease the heat of transition considerably below the 1000 cal. mole^{-1} estimate at the normal transition temperature. In any case it is believed that the measurements above 0° are representative of $ZnSO_4·6H_2O$ as such.

The Heats of Solution of $ZnSO_4·7H_2O$ and $ZnSO_4·6H_2O$.—The heat of solution of the "heptahydrate" was measured with another portion of the same material used for the low temperature heat capacity measurements. However, although precautions had been taken to assure uniform sampling, the sample had been kept for some time and the material was analyzed again to check the water content. Although the sample container was sealed with paraffin it was found that a small amount of water had been lost, leaving the over-all composition $ZnSO_4·6.938 H_2O$. The entrapped water was taken as 0.016 mole per mole of $ZnSO_4$, from the heat capacity measurements near the eutectic, which have been discussed above. This assumes no escape of the enclosed solution from the interior of the crystal. Thus the constitution of the samples corresponded to 0.922 mole $ZnSO_4·7H_2O$; 0.078 mole $ZnSO_4·6H_2O$; 0.016 mole H_2O.

However some of the $ZnSO_4·7H_2O$ must have dissolved in the water to form saturated solution at 25°. From the solubility data of Cohen and Hetterschij[15]

$$\frac{\text{moles } ZnSO_4}{\text{moles } H_2O} = 0.06410 \text{ (at } 25°) = \frac{x}{(0.016 + 7x)}$$

$xZnSO_4·7H_2O + 0.016\ H_2O$ contain $(0.016 + 7x)H_2O$ in solution where x represents the number of moles of $ZnSO_4·7H_2O$ in solution, which was found to be 0.00186. Thus the material actually dissolved had the form: 0.92014 mole $ZnSO_4·7H_2O$; 0.078 mole $ZnSO_4·6H_2O$; 0.00186 mole $ZnSO_4$ in saturated solution.

Had the crystals of heptahydrate been prepared with greater care the amount of entrapped solution could have been considerably reduced, however, the correction for the $ZnSO_4$ already in solution is not large and should not lead to appreciable error in the present case.

The above situation raises the question as to how often errors have entered heat of solution measurements due to the above cause. It is evident that the experimenter must present evidence other than an analysis showing that the total water present corresponds to the hydrate which he assumes to be present. We know of no previous case where this has been done. One of our co-workers suggests the name "brine holes" to cover such well known solution inclusions within crystals.

From the results of Giauque, Barieau and Kunzler[17] based in part on the present work the heat of the reaction

$$ZnSO_4·7H_2O + (A - 7)H_2O = ZnSO_4·AH_2O_{(\text{sat. soln.})} \quad \Delta H_{25°} = 5420 \text{ cal. mole}^{-1} \quad (4)$$

TABLE IV

HEAT OF SOLUTION DATA FOR "HEPTAHYDRATE," 25°

Run	1	2	3
Wt. sample *in vacuo*, g.	26.642	26.635	26.596
Mole $ZnSO_4$	0.09301	.09299	0.09285
Actual heat, cal.	369.81	372.06	371.02
Heat mole^{-1} $ZnSO_4$	3976	4001	3996
Heat mole^{-1} cor. for entrapped soln.	3986	4011	4006
	(av. 4001 ± 10 cal. mole^{-1} $ZnSO_4$		
G. H_2O at start	898	898	897
Moles H_2O/mole Zn	535.9	536.1	536.2
Moles H_2O from subst.	6.938	6.938	6.938
Total moles H_2O/mole Zn	542.8	543.0	543.1 (av. 543)

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[17] Giauque, Barieau and Kunzler, THIS JOURNAL, **72**, 5685 (1950).

For 0.00186 mole of $ZnSO_4$ forming a saturated solution the $\Delta H = 10$ cal.

Three heats of solution were measured on the "heptahydrate." The data are summarized in Table IV.

The sample of "hexahydrate" used for the measurements of its heat of solution was identical with that used for the low temperature heat capacity measurements

$$0.979 \text{ mole } ZnSO_4{\cdot}6H_2O + 0.021 \text{ mole } ZnSO_4{\cdot}7H_2O$$

The data are summarized in Table V.

TABLE V

HEAT OF SOLUTION DATA FOR "HEXAHYDRATE," 25°

Run	1	2	3
Wt. sample *in vacuo*, g.	25.002	24.988	25.045
Moles $ZnSO_4$	0.09263	0.09258	0.09279
Actual heat, cal.	82.71	82.46	82.65
Heat mole^{-1} cal.	892.9	890.7	890.7 (av. 891.4 ± 1.0)
G. H_2O at start	898.4	887.4	897.9
Moles H_2O/mole Zn	538.3	532.1	537.1
Moles H_2O from subst.	6.021	6.021	6.021
Total moles H_2O/mole Zn	544.3	538.1	543.1 (av. 542)

Since the concentrations of the final solutions are essentially the same for both the "heptahydrate" and "hexahydrate" the following equations may be combined.

$$0.922\ ZnSO_4{\cdot}7H_2O + 0.078\ ZnSO_4{\cdot}6H_2O + \text{water} = \text{Final solution} \quad \Delta H_{25°} = 4001 \quad (5)$$

$$0.021\ ZnSO_4{\cdot}7H_2O + 0.979\ ZnSO_4{\cdot}6H_2O + \text{water} = \text{Final solution} \quad \Delta H_{25°} = 891 \quad (6)$$

combining

$$ZnSO_4{\cdot}6H_2O + H_2O(l) = ZnSO_4{\cdot}7H_2O \quad \Delta H_{25°} = -3452 \text{ cal. mole}^{-1} \quad (7)$$

$$ZnSO_4{\cdot}7H_2O + 536H_2O(l) = ZnSO_4{\cdot}543H_2O(\text{solution}) \quad \Delta H_{25°} = 4270 \text{ cal. mole}^{-1} \quad (8)$$

It is of interest to mention what the above results would have been if the "brine holes" within the crystals had not been discovered. The values calculated are −3381 instead of −3452 and 4210 instead of 4270.

The Entropy of $ZnSO_4{\cdot}7H_2O$ from the Temperature Coefficient of the Clark Cell.—The reaction in the Clark cell is

$$Zn + Hg_2SO_4(s) + \frac{7}{A-7} ZnSO_4{\cdot}AH_2O(\text{satd. soln.}) = \frac{A}{A-7} ZnSO_4{\cdot}7H_2O(s) + 2Hg \quad (9)$$

$A_{25°} = 15.598$ moles H_2O/mole $ZnSO_4$.[15]

The thermodynamic investigation of the available data on the e.m.f. of the Clark cell at various temperatures, carried out by Giauque, Barieau and Kunzler,[17] with the assistance of their measurements of partial molal heat content and heat capacity of zinc sulfate solutions, shows that the work of Callendar and Barnes[18] is very self consistent. Giauque, Barieau and Kunzler[17] use the cell data to show that the $\int_0^T C_p \, d \ln T$ gives the correct entropy for $ZnSO_4{\cdot}7H_2O$ by a different method than the one utilized here.

The change in entropy accompanying the reaction in the Clark cell is given by the temperature coefficient. The entropies of all reactants and products are known, with the exception of the entropy of the saturated solution $ZnSO_4{\cdot}AH_2O$. This entropy can be obtained from the reactions

$$\frac{7}{A-7} ZnSO_4{\cdot}7H_2O(s) + 7H_2O(\text{satd. } ZnSO_4 \text{ soln.}) = \frac{7}{A-7} ZnSO_4{\cdot}AH_2O \quad (10)$$

$$\Delta F_{(10)} = 0$$

and

$$7H_2O = 7H_2O(\text{satd. } ZnSO_4 \text{ soln.}) \quad (11)$$

$$\Delta F_{(11)} = 7RT \ln (P_{H_2O}/P^{\circ}_{H_2O}) (\text{satd. } ZnSO_4 \text{ soln.})$$

where $P^{\circ}_{H_2O}$ refers to the vapor pressure of pure water at temperature T. Combining Equations 10 and 11

$$\frac{7}{A-7} ZnSO_4{\cdot}7H_2O(s) + 7H_2O = \frac{7}{A-7} ZnSO_4{\cdot}AH_2O \quad (12)$$

$$\Delta F_{(12)} = 7RT \ln (P_{H_2O}/P^{\circ}_{H_2O})(\text{satd. } ZnSO_4 \text{ soln.})$$

$P_{H_2O(\text{satd. } ZnSO_4 \text{ soln.})}/P^{\circ}_{H_2O}$ for $A = 15.598$ at 25° may be calculated from the measurement of Robinson and Jones.[19] Their results give $\Delta F_{(12)}/298.16 = -1.89$ cal. deg.$^{-1}$ mole^{-1}.

The heat of reaction, ΔH_{12}, corresponding to Equation 6 has been calculated by Giauque, Barieau and Kunzler,[17] by combining their measurements of the relative partial molal heat contents of zinc sulfate solutions up to saturation, with the similar data of Lange, Monheim and Robinson[20] for dilute solutions and the heat of solution data for $ZnSO_4{\cdot}7H_2O$ given above in Table IV.

$$\Delta H_{(12)} = 5420 \times \frac{7}{A-7} = 5420 \times \frac{7}{8.598} = 4413 \text{ cal. at } 298.16°\text{K.}$$

$$\Delta S_{(12)} = \frac{\Delta H_{(12)} - \Delta F_{(12)}}{T} = 16.69 \text{ cal. deg.}^{-1} \text{ at } 298.16°\text{K.}$$

The entropy of mercury has recently been recalculated by Pickard and Simon[21] who extended the earlier data to the liquid helium temperature range. They give $S_{Hg(25°)} = 18.48$ cal. deg.$^{-1}$ mole^{-1}. Keesom, van den Ende and Kok[22] have extended the heat capacity data on zinc to 1.3° K. and Kelley[23] has calculated the entropy from the various data. $S_{Zn(25°)} = 9.95$ cal. deg.$^{-1}$ mole.

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(18) Callendar and Barnes, *Proc. Roy. Soc.* (*London*), **62**, 117 (1897).

(19) Robinson and Jones, THIS JOURNAL, **58**, 959 (1936).

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

(21) Pickard and Simon, *Proc. Phys. Soc.*, **61**, 1 (1948).

(22) (a) Keesom and van den Ende, *Proc. Acad. Amster.*, **35**, 143 (1932); (b) Keesom and Kok, *Physica*, **1**, 770 (1933–1934).

(23) Kelley, U. S. Dept. of Inter., Bureau of Mines Bull. No. 394 (1935).

The entropy of Hg_2SO_4 has been determined by Schutz[24] from his unpublished measurements of heat capacity which extend to 15°K. Since a substance containing atoms of such large atomic weight requires the evaluation of a considerable amount of entropy by extrapolation, even from a temperature of 15°K., we decided to check the extrapolation. As we had access to the notebooks of the late Professor P. W. Schutz of this Laboratory, we worked from this source and could find no reason for changing his extrapolation estimate of 1.23 cal. deg^{-1} $mole^{-1}$ at 15.85°K., or his value of $S_{Hg_2SO_4} = 48.0$ cal. $deg.^{-1}$ $mole^{-1}$ at 25°. However it would be desirable to obtain measurements of the heat capacity of this substance in the liquid helium to liquid hydrogen temperature range.

Combining Equations 9 and 12, leads to the equation

$$Zn + Hg_2SO_4 + 7H_2O = ZnSO_4{\cdot}7H_2O + 2Hg \quad (13)$$

$$\begin{aligned}
\Delta S_{(13)} &= \Delta S_{(9)} + \Delta S_{(12)} \\
&= 2F\frac{dE}{dT} + \Delta S_{(12)} \\
&= 2 \times 23063 \times (-0.001340) + 16.69 \\
&= -61.8 + 16.69 \\
&= -45.11 \text{ cal. deg.}^{-1} \text{ per mole of } ZnSO_4{\cdot}7H_2O \\
S_{ZnSO_4 \cdot 7H_2O} &= \Delta S_{(13)} - 2S_{Hg} + 7S_{H_2O} + S_{Hg_2SO_4} + S_{Zn} \\
&= 93.0
\end{aligned}$$

The $\int_0^T C_p \, d \ln T$ for $ZnSO_4{\cdot}7H_2O$ is 92.9 cal. $deg.^{-1}$ $mole^{-1}$ in excellent agreement with the above value calculated from temperature coefficient of the Clark cell combined with heat of solution and other data. However, on account of the difficulty of evaluating dE/dT the close agreement must be considered fortuitous.

The value of $dE/dT = -0.001340$ volt $deg.^{-1}$ was selected by means of a graphical difference plot of the data of Callendar and Barnes,[18] after the much more reliable treatment of the cell data given in the following paper[17] had given us great confidence in the accuracy of Callendar and Barnes' measurements. The plot used was $E_t - E_{15°} + 0.00127\,t$.

In interpreting the data on the Clark cell we have made use of the experimental fact, due to Clayton and Vosburgh,[25] that electrodes of zinc and of saturated zinc amalgam have the same potential.

While the result here cannot be regarded as entirely independent of the results of Giauque, Barieau and Kunzler,[17] it is very satisfactory to have the continued very good agreement as supporting evidence when new data such as the heat of solution of $ZnSO_4{\cdot}7H_2O$ are brought into the thermodynamic framework.

The Entropy of $ZnSO_4{\cdot}6H_2O$ Calculated from the Free Energy and Heat of Hydration.—By means of the reaction $ZnSO_4{\cdot}6H_2O + H_2O = ZnSO_4{\cdot}7H_2O$ (7) the entropy of $ZnSO_4{\cdot}6H_2O$ may be calculated.

$$\Delta F_{(7)} = RT \ln (P_{H_2O}/P^{\circ}_{H_2O(l)})$$

where P_{H_2O} is the equilibrium pressure over the two hydrates.

The available data are summarized in Table VI.

TABLE VI

HYDRATION PRESSURE AT 25°C.

$$ZnSO_4{\cdot}6H_2O + H_2O_{(g)} = ZnSO_4{\cdot}7H_2O$$

P, mm.	Reference	Year
15.34	Schumb[26]	1923
15.38	Ishikawa and Murooka[27]	1930
15.38	Bannell and Burridge[28]	1935
15.3	Bell[29]	1940
15.35	Average	

$$\frac{\Delta F_{(7)}}{298.16} = 4.5761 \log \frac{15.35}{23.77} = -0.87 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$\frac{\Delta H_{(7)}}{298.16} = \frac{-3452}{298.16} = -11.58 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$\Delta S_{(7)} = \frac{\Delta H_{(7)} - \Delta F_{(7)}}{298.16} = -10.71 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$\begin{aligned}
S_{(ZnSO_4 \cdot 6H_2O)} &= -\Delta S_{(7)} - S_{(H_2O(l))} + S_{(ZnSO_4 \cdot 7H_2O)} \\
&= 10.71 - 16.73 + 92.91 \\
&= 86.9 \text{ cal. deg.}^{-1} \text{ mole}^{-1} \text{ at } 298.16°\text{K.}
\end{aligned}$$

The $\int_0^T C_p \, d \ln T$ for the hexahydrate may give an incorrect value for the entropy change over the interval due to the irreversible process which complicated the measurements. If the character and extent of the process were understood it might be possible to make a correction for it. We are inclined to assume that the process is not characteristic of metastable $ZnSO_4{\cdot}6H_2O$ since, as mentioned above, there was no evidence of an irreversible process of this kind when 6.7 mole % of $ZnSO_4{\cdot}6H_2O$ was included in the calorimeter with the "heptahydrate." Accordingly, the heat capacity of the $ZnSO_4{\cdot}6H_2O$ has been integrated, using the smooth curve which passes under the bulge and using the higher of the two sets of observations at very low temperatures.

$$\int_0^T C_p \, (ZnSO_4{\cdot}6H_2O) \, d \ln T = 85.1 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

If the bulge is included the value becomes 85.6 cal. $deg.^{-1}$ $mole^{-1}$.

Each of these values is considerably lower than the reliable value 86.9 cal. $deg.^{-1}$ $mole^{-1}$. Therefore, it is necessary to conclude that the substance in the calorimeter retained disorder at limiting low temperatures. Whether this is due to disorder caused by instability with respect to the mono- and heptahydrates or disorder due to hydrogen bond randomness cannot be decided on the basis of the evidence presented here.

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(24) Schutz, Thesis, Univ. of Calif. Berkeley, Calif., 1934.

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

(26) Schumb, *ibid.*, **45**, 342 (1923).

(27) Ishikawa and Murooka, *Bull. Inst. Phys. Chem. Res.* (*Tokyo*), **9**, 781 (1930).

(28) Bannell and Burridge, *Trans. Faraday Soc.*, **31**, 473 (1935).

(29) Bell, *J. Chem. Soc.*, 72 (1940).

The Heat of Transition of Zinc Sulfate Heptahydrate to Form the Hexahydrate and Saturated Solution at the Transition Temperature.—During the course of the heat capacity measurements on the "heptahydrate" the substance was heated through the transition temperature and the heat of transition was measured. It was not possible to check on the one observation since cooling the material could not be expected to restore the original phases within the calorimeter.

The solubility data of Cohen and Hetterschij[15] were extrapolated about 1° and gave a reliable value of $A = 12.944$ moles of water per mole of zinc sulfate in solution at the transition temperature which will be given below as 38.12°. Proceeding as was done in obtaining the composition of the sample for the heat of solution measurements, the composition at 38.12° prior to transition was as follows: 0.9303 mole $ZnSO_4 \cdot 7H_2O$; 0.0670 mole $ZnSO_4 \cdot 6H_2O$; 0.0027 mole $ZnSO_4$ in saturated solution due to entrapped water.

Immediately after transition the composition was 0.8633 mole $ZnSO_4 \cdot 6H_2O$; 0.1367 mole $ZnSO_4$ in saturated solution. The over-all process per mole of zinc sulfate was as follows: $0.8633 - 0.0670 = 0.7963$ mole of $ZnSO_4 \cdot 6H_2O$ formed from $ZnSO_4 \cdot 7H_2O$.

$0.9303 - 0.7963 = 0.1340$ mole of $ZnSO_4 \cdot 7H_2O$ dissolved to form saturated solution.

The total amount of heat absorbed at the transition temperature by the 0.58388 mole of zinc sulfate in the calorimeter was 2182.1 calories. Thus

$$0.9303\ ZnSO_4 \cdot 7H_2O = 0.7963\ ZnSO_4 \cdot 6H_2O + 0.1340\ ZnSO_4 \cdot AH_2O \quad (14)$$

$$\Delta H_{(\text{meas})\ 38.12^\circ} = \frac{2182.1}{0.58388} = 3737 \text{ cal.}$$

or

$$ZnSO_4 \cdot 7H_2O = \frac{A - 7}{A - 6} ZnSO_4 \cdot 6H_2O + \frac{1}{A - 6} ZnSO_4 \cdot AH_2O \quad (15)$$

$$\Delta H_{38.12^\circ} = 4017 \text{ cal. mole}^{-1}$$

Combining Equations 15 and 7 with the ΔH of the latter, corrected to 38.12°, the following results are obtained.

$$ZnSO_4 \cdot 6H_2O + (A - 6)H_2O_{(l)} = ZnSO_4 \cdot AH_2O \quad (16)$$

$$\Delta H_{311.28^\circ K.} = 2847$$

and

$$ZnSO_4 \cdot 7H_2O + (A - 7)H_2O_{(l)} = ZnSO_4 \cdot AH_2O \quad (17)$$

$$\Delta H_{311.28^\circ K.} = 6454$$

These last two values are not very accurate because they involve 6.944 times the difference of the quantities measured in the reactions corresponding to Equations 15 and 7.

Following the above measurement of the heat of transition, the transition temperature was studied. Energy was added in increments so that about 3, 25, 50 and 80% of the material had undergone transition. After equilibrium periods of several hours in each case the transition temperature was found to return to the same reading within 0.01°. The value was 311.28°K. ± 0.05°. This agrees well with values of 311.29 and 311.27°K. given by Cohen, Inouye and Euwen.[30] These latter values have been corrected to 0° = 273.16°K.

In a similar experiment $ZnSO_4 \cdot 6H_2O$ was heated to the transition point between the hexa- and monohydrates. This temperature was found to be 60.3°.

Acknowledgment.—We thank Drs. J. W. Stout and T. R. Rubin for assistance with the experimental measurements.

Summary

The heat capacities of zinc sulfate hepta- and hexahydrates have been measured from 15–300°K.

Their heats of solution have been determined at 25°.

The measurements on $ZnSO_4 \cdot 6H_2O$ were complicated by an irreversible effect which is discussed.

The heat of transition of $ZnSO_4 \cdot 7H_2O$ to form $ZnSO_4 \cdot 6H_2O$ and saturated solution at 38.12°, the transition temperature, has been found to be 4017 cal. mole^{-1}.

The entropy of $ZnSO_4 \cdot 7H_2O$ less nuclear spin and isotope effects, equals 92.9 cal. deg.^{-1} mole^{-1} at 298.16°, which agrees closely with a value obtained indirectly by means of the Clark cell.

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