JOURNAL OF THE
AMERICAN CHEMICAL SOCIETY
(Registered in U. S. Patent Office) (Copyright, 1955, by the American Chemical Society)

VOLUME 77 AUGUST 9, 1955 NUMBER 15

PHYSICAL AND INORGANIC CHEMISTRY

[CONTRIBUTION FROM THE LOW TEMPERATURE LABORATORY, DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF CALIFORNIA, BERKELEY]

The Spontaneous Transformation from Macrocrystalline to Microcrystalline Phases at Low Temperatures. The Heat Capacity of $MgSO_4 \cdot 6H_2O$[1]

BY W. P. COX, E. W. HORNUNG AND W. F. GIAUQUE

RECEIVED MARCH 7, 1955

The heat capacity of $MgSO_4 \cdot 6H_2O$ has been measured from 15 to 325°K. Assuming crystal perfection at 0°K. the entropy at 298.16°K. was found to be 83.20 cal. deg.$^{-1}$ mole^{-1}. A table of thermodynamic properties from 0 to 320°K. has been presented. These results were obtained when the sample was not allowed to stand near 120°K. for more than a short period. When $MgSO_4 \cdot 6H_2O$ is allowed to stand in the region near 120°K. heat is slowly evolved. Heat capacity measurements starting at 15°K., on sample thus treated, disclosed no anomaly near 120° and absorption of heat over a broad region with a maximum near 246°K. Nitrogen gas adsorption near 77°K. showed that the evolution of heat was accompanied by the formation of microscopic phase regions. Barieau, Chu and Giauque had found that $ZnSO_4 \cdot 6H_2O$ behaves in an almost identical manner. The two crystals are isomorphous. Zinc sulfate hexahydrate has been reported by Copeland and Short to be unstable with respect to the reaction $6ZnSO_4 \cdot 6H_2O = 5ZnSO_4 \cdot 7H_2O + ZnSO_4 \cdot H_2O$ below 21.5°. Thus the most plausible explanation of the anomalous heat effects in both the zinc and magnesium hexahydrates is to assume their decomposition into other hydrates, a process so difficult in the solid state that only microcrystalline phase regions can be formed. The ΔH of the reaction $MgSO_4 \cdot 7H_2O = [(A - 7)/(A - 6)]MgSO_4 \cdot 6H_2O + [1/(A - 6)]MgSO_4 \cdot AH_2O(l)$ was found to be 4789 cal. mole^{-1} at the transition temperature 48.15°. A was taken equal to 15.595.

The entropies of numerous hydrated substances have been measured in this Laboratory as a means of detecting possible frozen-in crystalline disorder due to hydrogen bonding. During one of these investigations Barieau and Giauque[2] found anomalous thermal behavior near 250°K. in $ZnSO_4 \cdot 6H_2O$. This was interpreted as due to the reaction

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

in the solid state, since Copeland and Short[3] had found that $ZnSO_4 \cdot 6H_2O$ is unstable with respect to these phases below 21.5°. The transportation of water in the solid state is obviously so difficult, that Barieau and Giauque[2] concluded that only microcrystalline phase regions of the mono- and heptahydrates could be formed in such a process. Since the free energy of the microscopic phases would be considerably higher than that of macroscopic material, it was not surprising that the transition was lowered to about 250°K. Also the fact that the transition region was broad is in accord with the expectations of a range of microphase sizes.

Later unpublished work in this Laboratory by Chu and Giauque disclosed additional information about the $ZnSO_4 \cdot 6H_2O$ system. They found that when this substance was cooled to temperatures above 120°K., no transformation occurred, but between 70 and 120°K. there was heat evolution with a maximum rate near 95°K. The heat absorption for the reverse process occurred over a range near 250°K., as had been found by Barieau and Giauque. Chu and Giauque concluded that in order to surmount the free energy barrier involved in the starting of microscopic phase regions it was necessary to supercool the unstable hexahydrate to about 100°K. After the initial phase regions were formed, later growth raised the transition temperature of the larger, yet still microcrystalline, phase regions to about 250°K. They supported this idea by means of gas adsorption measurements performed through the cooperation of Professor G. Jura. These showed that the heat evolution near 100°K. was accompanied by a large increase in surface to between 1 and 2 square meters per g. This was considered to be only a small portion of the interfacial surface between the microphase regions since it seems unlikely that more than a minor part of the interfacial area would be accessible for gas adsorption.

---

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

(2) R. E. Barieau and W. F. Giauque, THIS JOURNAL, **72**, 5676 (1950).

(3) L. C. Copeland and O. A. Short, *ibid.*, **62**, 3285 (1940).

The whole subject of crystal perfection is of basic importance to the investigation and interpretation of magnetic and other properties in the temperature range near and below 1°K. It is obviously futile to spend long periods growing large single crystals, and additional effort cutting shapes such as ellipsoids of revolution about crystal axes of interest, unless it has been shown that the hydrate will not undergo some rearrangement during cooling. The type of phenomenon discussed here is more serious because it will affect even measurements on powdered crystals. The properties of material dispersed in microcrystalline phase regions should be appreciably different from those of macroscopic crystals at temperatures below 1°K. The situation will be even more complicated if microcrystalline phases of two different hydrates are intermixed. In the case of $ZnSO_4 \cdot 6H_2O$, cooled with moderate rapidity, the evidence suggests a mixture of unconverted macrocrystalline $ZnSO_4 \cdot 6H_2O$, microcrystalline $ZnSO_4 \cdot 7H_2O$, and microcrystalline $ZnSO_4 \cdot H_2O$, when the material reaches very low temperatures. Zinc sulfate hexahydrate is not paramagnetic but has been studied because it has structural similarities to other hydrated sulfates of the iron group, without the entropy complications due to their electronic systems.

It is suggested that investigations of paramagnetic substances at very low temperatures should be preceded by a very careful investigation of the thermal properties over the whole range of temperature.

The present work was undertaken on $MgSO_4 \cdot 6H_2O$ because it is isomorphous[4] with $ZnSO_4 \cdot 6H_2O$. They are monoclinic. It was found that the $MgSO_4 \cdot 6H_2O$ acted in almost the same manner as $ZnSO_4 \cdot 6H_2O$ except that it proved possible to cool it rapidly to 15°K. without allowing the microphases to form, as well as to produce them at will. Chu and Giauque, in the work mentioned above, had tried rapid cooling but were only partially successful in avoiding the formation of the microphase regions.

Preparation of $MgSO_4 \cdot 6H_2O$.—A solution of magnesium sulfate (Mallinckrodt Analytical Reagent), saturated at 55°, was prepared. After heating to 65° and filtering it was transferred to a flask in a 55° thermostat and seeded with crystals of $MgSO_4 \cdot 6H_2O$. By slow evaporation crystals were grown over a period of three months at 55°.

The crystals, some of which were over a centimeter in length, were roughly dried by means of a stream of pure dry air and then broken up before being placed in the calorimeter. Representative samples, taken during the filling of the calorimeter, were analyzed by dehydration. The samples were reduced to monohydrate by slowly raising the temperature to 150° over a period of several days, and then heated to constant weight at 430–450°. The dehydration of the monohydrate required about 4 days but the heating was continued for about a week. One sample, which was held at 440° for 74 days, retained the same weight that it had attained after a week at this temperature.

The over-all composition of the substance investigated was found to be $MgSO_4 \cdot 6.0277H_2O$. The calorimeter contained 151.79 g. of this material. Thus the calorimeter contained 0.6445 mole of $MgSO_4 \cdot 6H_2O$ and 0.0184 mole of $MgSO_4 \cdot 7H_2O$. The molecular weight of $MgSO_4 \cdot 6H_2O$ was taken as 228.48.

The fact that the crystals were free of solution inclusion was shown by the absence of any eutectic melting or heat of solution effects in preliminary heat capacity measurements, made for that purpose, in the region below 0°.

The results of the dehydration analysis were confirmed calorimetrically in the following manner: The heat of the reaction

$$MgSO_4 \cdot 7H_2O(s) = \frac{A-7}{A-6} MgSO_4 \cdot 6H_2O(s) + \frac{1}{A-6} MgSO_4 \cdot AH_2O(l) \quad (2)$$

was determined in a separate experiment to be $\Delta H_{48.15°} = 4789$ cal. mole^{-1}. The value of A was taken from the solubility curve given by Seidell.[5] $A = 15.595$ moles H_2O per mole of $MgSO_4$ in a saturated solution at the transition temperature, which was determined to be 48.15°.

The heat of the above reaction was determined by means of an experiment in which 0.5744 mole of $MgSO_4 \cdot 7H_2O$ with 0.0075 mole of excess water was placed in the calorimeter and heated through the transition.

On the basis of one mole of $MgSO_4$ the process for the above mixture can be calculated to be 0.9985 mole $MgSO_4 \cdot 7H_2O$ + 0.0015 mole $MgSO_4$ in sat. soln. = 0.8944 mole $MgSO_4 \cdot 6H_2O$ + 0.1056 mole $MgSO_4$ in sat. soln. $\Delta H_{48.15°} = 4782$ cal. mole^{-1} $MgSO_4$ measured. The heat of transition of pure $MgSO_4 \cdot 7H_2O$, as given in equation 2, may be calculated to be $\Delta H_{48.15°} = 4789$ cal. mole^{-1}.

It was found that the sample of "hexahydrate" in the calorimeter absorbed 133 calories per mole of $MgSO_4$ at 48.15°, which gives 0.0185 mole $MgSO_4 \cdot 7H_2O$, in almost exact agreement with the 0.0184 value from the analysis.

Apparatus and Temperature Scale.—The heat capacity measurements were made in a calorimeter similar to the one used by Giauque and Archibald.[6] Calibration of the gold resistance thermometer–heater was carried out concurrently with the heat capacity measurements by means of a standard copper–constantan thermocouple with the laboratory designation W-26.[7] The thermocouple was attached to the calorimeter mechanically, as described by Busey and Giauque,[8] because the temperature necessary for soldering might have caused extensive hydrate decomposition.

After Series 6 of the heat capacity measurements, to be given below, the thermocouple was compared with the triple and boiling points of hydrogen and nitrogen. This was done, as is usual in this Laboratory for this type of calorimeter, by condensing the appropriate gas in the insulating vacuum space, and thus in direct contact with the calorimeter. The thermocouple read 0.01° low at the triple point (13.92°K.) of hydrogen and 0.02° high at its boiling point (20.36°K.). It agreed with the original calibration at the triple point (63.15°K.), and boiling point (77.34°K.) of nitrogen.

One defined calorie was taken equal to 4.1840 absolute joules. 0°C. was taken to be 273.16°K.

The Heat Capacity of $MgSO_4 \cdot 6H_2O$.—To obtain the heat capacity of pure $MgSO_4 \cdot 6H_2O$ it was necessary to correct for the 0.0184 mole of $MgSO_4 \cdot 7H_2O$ in the calorimeter. The heat capacity of the heptahydrate was obtained from some preliminary measurements over the range 15–300°K. The sample contained excess water and a small amount of $MgSO_4 \cdot 12H_2O$ was formed. The presence of the dodecahydrate, of unknown heat capacity, reduced the accuracy to which the heat capacity of the heptahydrate could be calculated; however it was known to at least 1% which is sufficiently accurate for the correction in the case of the hexahydrate.

It was eventually found that the hexahydrate evolved heat when held in the range 100–140°K. and when this has occurred there is subsequent heat absorption in the range above 235°K. The effect had essentially disappeared by 285°K.

Series 1.—The sample was cooled from room temperature directly to 14°K. The rate of cooling at 140°K. was 1° min.$^{-1}$. The subsequent heat capacity measurements were normal until 120°K. at which point heat evolution be-

---

[4] F. Hammel, *Ann. chim.*, [11] **11**, 247 (1939).

[5] A. Seidell, "Solubilities of Inorganic and Metal Organic Compounds," 3rd Edition, Vol. 1, D. Van Nostrand Co., Inc., New York, N. Y., 1940, p. 985.

[6] W. F. Giauque and R. C. Archibald, This Journal, **59**, 561 (1937).

[7] W. F. Giauque and C. J. Egan, *J. Chem. Phys.*, **5**, 45 (1937).

[8] R. H. Busey and W. F. Giauque, This Journal, **74**, 4443 (1952).

TABLE I

HEAT CAPACITY OF $MgSO_4 \cdot 6H_2O$

Cal. deg.$^{-1}$ mole^{-1}; mol. wt. = 228.48; 0°C. = 273.16°K.

T, °K.	ΔT, approx.	C_p
Series 1		
14.55	1.42	1.26
15.96	1.26	1.61
17.51	1.78	1.98
19.31	1.67	2.44
21.67	2.61	3.17
24.61	3.17	4.19
28.26	4.12	5.52
32.24	3.84	7.01
36.32	4.22	8.53
40.77	4.53	10.23
45.60	5.05	12.14
51.02	5.74	14.37
56.69	5.56	16.68
62.15	5.26	18.79
67.26	4.99	20.70
72.70	5.84	22.66
78.75	6.21	24.78
85.77	7.76	27.12
99.73	6.70	31.72
106.96	7.70	34.02
114.39	6.94	36.22^a
121.23	5.76	38.03^a
127.55	5.48	40.04^a
132.90	5.12	41.66^a
138.70	6.38	43.58
145.34	6.80	45.48
152.05	6.56	47.67
158.81	6.90	49.67
165.90	7.20	51.75
173.22	7.32	53.88
180.45	7.01	55.89
187.63	7.20	57.71
194.78	6.88	59.75
201.81	7.10	61.66
208.90	6.82	62.98
215.95	8.10	65.16
223.25	7.36	66.80
230.40	6.80	68.52
237.43	7.10	71.62^b
244.02	6.06	84.50^b
249.38	4.90	81.17^b
254.89	6.22	77.54^b
261.40	6.74	76.57^b
268.60	7.09	77.37^b
275.99	7.32	78.86
283.64	7.58	80.23
291.59	7.74	82.50
299.44	7.45	83.60
Series 2		
193.22	7.87	59.38
201.30	8.08	61.47
210.00	9.07	63.64
219.31	9.24	66.03
228.77	9.34	68.20
238.00	8.87	70.48
247.82	9.04	72.71
262.41	8.30	75.67
271.40	9.09	77.67
280.50	8.65	79.49
289.57	8.80	81.61
298.56	8.42	83.21
Series 3		
142.76	6.82	44.99
149.75	7.08	47.14
157.04	7.41	49.28
164.60	7.59	51.49
172.32	7.74	53.70
180.25	7.94	55.93
188.37	8.06	58.08
196.95	8.94	60.33
206.14	9.17	62.69
215.47	9.29	64.98
224.58	8.72	67.29
233.53	8.90	68.54
242.71	9.05	71.50
252.06	9.27	73.58
261.81	9.42	75.64
271.56	9.66	77.74
281.30	9.19	79.60
290.22	7.92	81.85
298.24	7.59	83.40
Series 4		
15.35	1.40	1.45
16.77	1.34	1.79
18.48	2.07	2.24
21.07	3.12	2.99
24.19	3.01	4.04
27.92	4.22	5.38
32.28	4.36	7.02
36.84	4.66	8.74
41.68	4.94	10.58
47.18	5.94	12.78
53.18	6.05	15.24
59.17	5.88	17.64
64.91	5.57	19.81
70.84	6.25	21.99
77.01	6.06	23.89
83.29	6.48	26.29
90.01	6.93	28.54
96.90	6.81	30.82
103.90	7.22	33.07
111.09	7.13	35.30
124.01	5.90	39.27
130.15	6.27	41.11
136.57	6.53	43.08
143.30	6.86	45.21
150.28	7.07	47.33
164.05	6.99	51.31
171.22	7.27	53.38
178.69	7.57	55.50
186.40	7.80	57.53
194.02	7.33	59.55
201.59	7.67	61.61
209.11	7.25	63.43
216.61	7.56	65.32
224.01	7.04	67.09
231.00	6.72	68.73
237.71	6.43	70.49
244.10	6.16	71.99
250.78	6.98	73.39
258.40	8.02	74.98
266.76	8.41	76.69
275.00	7.87	78.33
283.23	8.11	79.97
291.39	7.74	81.91
299.83	8.14	83.56
Series 5		
13.97	2.10	0.86
15.82	1.54	1.21
17.78	2.18	1.65
20.81	3.49	2.45
24.05	2.83	3.45
27.53	3.88	4.68
31.41	3.77	6.10
35.54	4.40	7.65
39.95	4.37	9.34
44.56	4.77	11.16
49.71	5.43	13.27
55.19	5.47	15.47
60.72	5.52	17.64
66.52	6.03	19.86
72.78	6.44	22.22
79.09	6.16	24.46
85.18	6.02	26.52
91.17	5.96	28.50
97.60	6.89	30.59
104.47	6.84	32.78
111.49	7.21	35.04
118.68	7.17	37.33
125.83	7.10	39.53
133.00	7.22	41.73
140.27	7.29	43.95
147.75	7.63	46.22
155.23	7.23	48.45
162.65	7.52	50.64
169.97	7.02	52.76
177.19	7.31	54.84
184.35	6.85	56.79
191.47	7.17	58.68
198.94	7.44	60.68
206.20	7.06	62.44
213.66	7.35	64.21
220.94	6.99	65.89
227.87	6.66	67.60
234.05	5.10	69.16
239.06	4.73	73.06^b
243.46	4.08	86.16^b
247.64	4.20	93.93^b
252.17	4.98	84.47^b
257.05	5.27	79.64^b
262.36	5.68	79.04^b
267.95	5.58	78.65^b
273.90	6.08	79.13^b
280.11	6.51	80.19^b
286.73	7.00	80.78
294.00	7.23	82.48
301.60	7.48	83.82
308.21	5.41	85.24
313.76	5.26	86.36
Series 6		
311.46	5.91	85.85
317.14	5.02	87.12
321.90	4.35	119.48^c
325.77	3.33	88.89
Series 7		
221.26	7.05	66.38
229.31	8.71	68.31
238.23	8.91	70.36
247.36	9.11	72.38
256.75	9.18	75.23
266.13	9.42	76.47
275.83	9.66	78.51
285.73	9.84	80.42
295.85	9.98	82.47

[a] Heat evolution. [b] Slow thermal equilibrium. [c] Heptahydrate transition; ΔT = 4.347.

gan. After 21 hours of heat evolution, heat was added until a temperature of 140°K. was reached and heat evolution ceased. The heat capacity measurements were resumed and there were no unusual phenomena until 235°K. Between 235 and 265°K. about 154 cal. mole^{-1} of hexahydrate were absorbed in excess of the normal heat capacity.

The general pattern showed a close resemblance to the thermal behavior of $ZnSO_4 \cdot 6H_2O$.

Series 2.—The sample was heated to about 45° (the transition temperature is 48.15°) to promote reconversion, if necessary, to its original form, and later cooled to about 190°K. The heat capacity between 190 and 300°K. was entirely normal with no anomalous heat absorption in the range above 235°K.

Series 3.—The sample was cooled to 140°K. and the results checked those obtained in series 2 but were consistently higher than the measurements of series 1 by about 0.4%.

Series 4.—The sample was cooled from room temperature to 14°K., as rapidly as was possible, considering the heavy enclosing lead-copper cylinder. The rate at 140°K. was about 3°min.$^{-1}$. The results agreed well with those of series 1 up to 120°K. and with those of series 2 and 3 between 140 and 300°K., except that the results were several tenths of a per cent. low between 120 and 140°K. and as much as 0.3% high between 240 and 270°K. This indicated that the transformation would have occurred had time been allowed.

Series 5.—The sample was cooled to approximately 80°K. and allowed to warm slowly to about 120°K. over a period of a week. Heat evolution was noted near 120°K. The calorimeter was held near 120°K. for over a week and no further heat evolution could be detected.

The calorimeter was then cooled to the temperature of liquid hydrogen and allowed to warm slowly to 120°K. over a period of a week and no further heat evolution could be detected.

The calorimeter was cooled to 13°K. and the heat capacity measurements of series 5 were obtained up to 316°K. The results paralleled those of series 4 but were about 0.5 cal. deg.$^{-1}$ mole^{-1} lower. There was no spontaneous heat evolution during these measurements. Above 235°K. there was anomalous heat absorption, with a maximum near 246°K. The total excess heat absorption above 235°K. was about 278 cal. mole^{-1} of $MgSO_4 \cdot 6H_2O$. Above 285°K. the results agreed with those of series 4, indicating that the substance had returned to its normal condition. In the range of anomalous heat absorption, thermal equilibrium was very slow and observations were taken for as long as four hours in several cases. The measured rate of change of temperature with time, less the effect due to heat lost to the surroundings was found to be logarithmic with time. Accordingly these measurements were calculated as described by Barieau and Giauque.[2] Slow equilibrium is to be expected in the kind of process which is believed to occur here.

Series 6.—After standing for about seven weeks near 293°K. a series of measurements through the transition temperature 48.15° was made to check the water analysis as mentioned above.

At this point the calorimeter was cooled to the temperatures of liquid hydrogen for the thermocouple calibrations mentioned above. After the calibrations it was warmed to about 310°K. to ensure reconstitution of the original substance.

Series 7.—The sample was held between 205 and 220°K. for a month, to invite any possible transformation. Subsequent measurements over the range 220–300°K. gave good agreement with normal measurements in series 2, 3 and 4, and indicated that no transformation had occurred.

Series 8.—This was another short run through the 48.15° transition of the $MgSO_4 \cdot 7H_2O$ to again check the analysis.

Following series 8 the calorimeter was cooled to about 115°K. and allowed to stand for 28 days to make sure that heat evolution was complete. It was then warmed slowly to about 200°K. over a period of 30 days and allowed to remain at about 200°K. for an additional 60 days. The heat capacity through the anomalous region was found to be approximately the same as that found in series 5 except that the maximum was about 5° lower. The purpose of this experiment had been to see whether long standing at 200°K. would allow the substance to make a closer approach to macroscopic phases and raise the temperature of the transition region. The lowering of the temperature may have been due to the fact that the sample was not subjected to double cooling with liquid hydrogen as was done before series 5. The data of this last experiment are not included.

The observations are given in Table I. They are corrected for the small amount of $MgSO_4 \cdot 7H_2O$ present. The thermodynamic properties of macroscopic crystalline $MgSO_46 \cdot H_2O$ are presented in Table II.

Table II

Thermodynamic Properties of Magnesium Sulfate Hexahydrate, Cal. Deg.$^{-1}$ Mole^{-1}

T, °K.	C_p	S	$\frac{H° - H°_0}{T}$	$\frac{(F° - H°_0)}{T}$
15	1.37	0.49	0.33	0.16
20	2.66	1.06	0.74	0.32
25	4.32	1.82	1.29	0.53
30	6.13	2.77	1.94	0.83
35	8.02	3.86	2.68	1.18
40	9.93	5.05	3.46	1.59
45	11.89	6.33	4.29	2.04
50	13.93	7.69	5.15	2.54
60	17.96	10.59	6.96	3.63
70	21.68	13.64	8.80	4.84
80	25.18	16.77	10.63	6.14
90	28.53	19.93	12.43	7.50
100	31.81	23.11	14.21	8.90
110	34.99	26.29	15.95	10.34
120	38.10	29.47	17.67	11.80
130	41.18	32.64	19.36	13.28
140	44.23	35.80	21.03	14.77
150	47.24	38.96	22.67	16.29
160	50.19	42.10	24.30	17.80
170	53.05	45.23	25.91	19.32
180	55.83	48.34	27.50	20.84
190	58.52	51.43	29.06	22.37
200	61.13	54.50	30.60	23.90
210	63.68	57.54	32.11	25.43
220	66.15	60.56	33.60	26.96
230	68.53	63.56	35.07	28.49
240	70.84	66.52	36.51	30.01
250	73.06	69.46	37.93	31.53
260	75.21	72.37	39.32	33.05
270	77.32	75.25	40.69	37.56
280	79.42	78.10	42.04	36.06
290	81.51	80.92	43.36	34.56
298.16	83.20	83.20	44.42	38.74
300	83.59	83.72	44.67	39.05
310	85.67	86.49	45.96	40.53
320	87.74	89.24	47.23	42.01

Increase of Surface at Low Temperatures.—In order to confirm that the formation of microscopic phase regions accompanied the heat evolution when $MgSO_4 \cdot 6H_2O$ was held near 120°K., gas adsorption measurements were made. A sample of the hexahydrate, held at 195°K., was degassed for five days by means of a mercury diffusion pump. The sample was then cooled to 77°K., and the surface measured by nitrogen adsorption. The method of Harkins and Jura[9] was used to calculate the extent of exposed interface. The surface was probably incompletely degassed and only a small portion of the interface area between the microscopic phase regions would be expected to be accessible for gas adsorption. A value of 1.1 square meters per gram was found.

The Entropy of $MgSO_4 \cdot 6H_2O$.—The data of series 4 may be used to calculate $\int_0^{228.16} C_p \, d \ln T$ for $MgSO_4 \cdot 6H_2O$. The result, including a Debye extrapolation of 0.49 cal. deg.$^{-1}$mole^{-1} below 15°K., is 83.20 cal. deg.$^{-1}$mole^{-1}.

The data of series 5, following maximum opportunity for heat evolution near 120°K., were also used to evaluate the entropy change. The $\int_0^{298.16} C_p \, d \ln T$, including an amount of 0.37 cal. deg.$^{-1}$mole^{-1} from a Debye extrapolation below 15°K., was found to be 82.94 cal. deg.$^{-1}$mole^{-1}.

The entropy discrepancy 83.20 − 82.94 = 0.26 cal. deg.$^{-1}$ mole^{-1} is not large and indicates that the transition from the microcrystalline condition made a fair approach to a reversible process.

Discussion.—The very marked similarity in the low temperature behavior of $MgSO_4 \cdot 6H_2O$ and $ZnSO_4 \cdot 6H_2O$ strongly suggests that the same explanation applies to both cases. The known instability of $ZnSO_4 \cdot 6H_2O$ with respect to decomposition into the hepta- and monohydrates offers the most plausible explanation. The stability relationships of the magnesium sulfate hydrates are unavailable. If later experiment shows that $MgSO_4 \cdot 6H_2O$ is stable with respect to decomposition into other hydrates in the region just above the anomalous heat absorption some other explanation of the formation of micro phases would be necessary. The formation of another modification of the hexahydrates, involving a rather complete rearrangement of the molecules, could produce the fractured situation sometimes exhibited by pseudomorphic crystals. An X-ray crystal structure determination at a sufficiently low temperature would probably decide whether one or more hydrated forms are present. The fact that the heat capacity of the microscopic form is about 0.5 cal. deg.$^{-1}$mole^{-1} below that of the ordinary $MgSO_4 \cdot 6H_2O$ at temperatures below 200°K. is consistent with what would be expected following conversion into one or more stable crystalline forms. The mere fracturing of a crystal into the microscopic state would be expected to increase heat capacity.

We thank D. L. Hildenbrand for assistance with the heat capacity measurements and Professor G. Jura and Hartland Schmidt for assistance with the adsorption measurements.

Berkeley, California

---

(9) W. D. Harkins and G. Jura, This Journal, **66**, 1366 (1944).