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

The Heat Capacity and Entropy of Sulfuric Acid Trihydrate Glass and Crystals from 15 to 300°K.[1]

BY J. E. KUNZLER AND W. F. GIAUQUE

The heat capacity of $H_2SO_4·3H_2O$ has been measured in the crystalline and supercooled glass and liquid forms from 15 to 300°K. The temperature of the transition $H_2SO_4·3H_2O = H_2SO_4·4H_2O$ + Liquid is 236.72 ± 0.05°K. The heat of fusion was found to be 5782 cal. mole^{-1} at the transition temperature. The entropy less nuclear spin and isotope effects is 82.90 cal. deg.$^{-1}$ mole^{-1}. At 0°K. the glass retains an amount of disorder corresponding to 5.9 cal. deg.$^{-1}$ mole^{-1} of entropy.

The research reported here is part of the investigation in progress in this Laboratory[2] on the thermodynamics of aqueous sulfuric acid. We are particularly interested in determining whether residual entropy exists at limiting low temperatures due to random hydrogen bonding or other types of disorder. Since sulfuric acid solutions supercool easily, measurements on the glass, as well as on the crystals, were obtained.

The low temperature measurements were made in an apparatus described previously[3,2] as Gold Calorimeter III. The standard thermocouple, with the laboratory designation W-25, which was used in conjunction with the gold resistance thermometer was rechecked against the boiling points of hydrogen and nitrogen. It was found to read 0.12° high at 20.36°K. and 0.02° low at 77.32°K. Appropriate corrections were made. One cal. was taken as 4.1833 international joules and 0°C. = 273.16°K. The sulfuric acid trihydrate was made by diluting 96% reagent grade acid. Since $H_2SO_4·3H_2O$ has an unstable melting point, eutectic heat effects could not be used in a simple manner as a test of purity. Accordingly the trihydrate was adjusted as carefully as possible to that composition by analysis. Later refinement of the analysis of sulfuric acid based on very thorough investigation of various methods[4] showed that the sample actually contained excess acid equivalent to 0.07 mole % dihydrate.

Heat Capacity Measurements on Glass and Liquid.—The $H_2SO_4·3H_2O$ sample in the calorimeter was first cooled to liquid hydrogen temperatures as a glass. Measurements of heat capacity, given as Series 1, Table I, proceeded in the normal manner until temperatures near 152°K. where about 26 cal. mole^{-1} of heat were evolved. This heat corresponds to energy changes characteristic of annealing of glasses. A similar effect can be observed in glycerine glass[5] although in that case the process is so much slower that it was possible to take heat capacity measurements rapidly enough so that little, if any, annealing occurred. This effect occurs just before the typical rapid increase in heat capacity in each case (Fig. 1). The effect could be distinguished from the start of crystallization due to the fact that measurements to higher temperatures were without any abnormal heat effects. At a temperature of about 180°K. crystallization started and proceeded rapidly. This occurred well above the region of rapid rise in heat capacity which occurs at about 158°K.

After the measurements given as Series 1, Table II, on the crystalline material, the sample was heated to about 50° and allowed to cool to room temperature several times to break up any crystalline aggregates which might have persisted in the liquid or on a surface. The liquid was then cooled to about 178°K. and one measurement, given as Series 2 of Table I, was obtained. The material then recrystallized. The sample was again heated to about 50° and treated as above. It was then cooled to about 205°K. and the results of Series 3, Table I were obtained over a range which extended above the melting point. Series 4 consists of measurements on the liquid above the melting point. The measurements on the stable and supercooled liquid are given in Table I.

TABLE I

HEAT CAPACITY IN CAL. DEG.$^{-1}$ MOLE^{-1} OF GLASS AND LIQUID $H_2SO_4·3H_2O$

0°C. = 273.16°K.

$T_{av.}$, °K.	ΔT, approx.	C_p
	Series 1	
16.00	2.8	1.60
18.85	2.6	2.42
21.13	2.0	3.06
23.74	3.3	3.84
27.06	3.0	4.93
30.31	3.3	5.81
33.33	2.8	6.71
36.52	3.4	7.54
39.89	3.3	8.64
43.38	3.6	9.25
47.03	3.8	10.49
51.01	4.1	11.49
56.69	3.5	12.87
60.38	3.9	13.72
64.27	4.0	14.65
68.51	4.5	15.53
72.75	3.9	16.42
76.89	4.4	17.22
81.65	5.0	18.02
86.98	5.8	18.96
92.58	5.3	19.89
98.61	6.8	20.90
104.74	5.4	21.87
110.14	5.3	22.76
115.98	6.5	23.67
122.08	5.4	24.64
127.78	5.9	25.54
134.36	7.3	26.61
141.33	7.4	27.80
148.73	6.8	29.22
152.03	6.5	30.06
157.66	4.9	49.37
161.77	3.9	73.18
166.23	5.1	73.47
171.65	5.7	73.61
177.28	5.5	73.77
	Series 2	
181.74	5.9	73.94
	Series 3	
210.33	10.5	73.76
220.53	10.0	74.06
229.64	7.7	74.01
237.25	7.5	74.08
	Series 4	
244.43	8.0	74.35
252.99	8.5	74.58
261.39	8.2	74.81
270.31	8.5	75.20
278.83	8.0	75.51
287.87	9.2	75.96
297.62	9.5	76.60

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[1] This research was supported in part by the Office of Naval Research, United States Navy.

[2] T. R. Rubin and W. F. Giauque, THIS JOURNAL, **74**, 800 (1952).

[3] W. F. Giauque and C. J. Egan, *J. Chem. Phys.*, **5**, 45 (1937); ref. 2.

[4] J. E. Kunzler, paper to be published.

[5] G. E. Gibson and W. F. Giauque, THIS JOURNAL, **45**, 93 (1923).

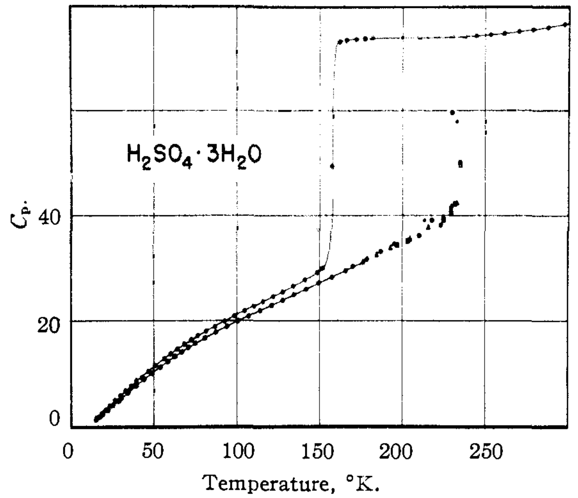

Fig. 1.—Heat capacity of $H_2SO_4 \cdot 3H_2O$: C_p in calories mole^{-1} degree^{-1}. Liquid and glass: ⊙, series I; △, series II; ⊡, series III; ⊖, series IV. Crystals: ●, series I; ▲, series II; ■, series III.

Heat Capacity of $H_2SO_4 \cdot 3H_2O$ Crystals.—The formation of crystalline sulfuric acid trihydrate in a calorimeter raised special problems due to its unstable melting point. At a temperature about 0.1° below the melting point the trihydrate is in equilibrium with tetrahydrate and solution as was discovered by Gable, Betz and Maron,[6] who also gave the temperature–composition diagram.

When crystallization occurred in the glass, at the end of Series 1, Table I, the heat evolved raised the temperature to the transition at 236.72°K. It was possible to compute, from the heat content of substance plus calorimeter, that 76% of the substance was solid trihydrate and that 24% remained in the liquid form. The calorimeter and contents were then cooled slowly to liquid nitrogen temperatures, and later to the temperatures of liquid hydrogen. The heat capacity was then measured. The results are given as Series 1 of Table II. Preliminary examination of the data indicated that heat had been absorbed at both the mono-tetrahydrate eutectic and the di-trihydrate eutectic showing that small amounts of these substances were present. This is not particularly surprising in view of the observations of Gable, Betz and Maron[6] who showed (their Fig. 2) that at compositions below these eutectics it was possible to have a liquid which was supersaturated with respect to mono-, di-, tri- and tetrahydrates. We never succeeded in crystallizing sulfuric acid trihydrate without the formation of some tetrahydrate and it is not surprising that some formed when the sample was cooled from the transition temperature where the tetrahydrate is in equilibrium with the trihydrate and liquid.

The formation of tetrahydrate from a liquid with the over-all composition corresponding to trihydrate must leave an acid rich liquid phase. When this is cooled some di- or monohydrate or both will be produced. In Series 1 both happened to crystallize, presumably in different portions of the calorimeter.

Table II

Heat Capacity in Cal. Deg.$^{-1}$ Mole^{-1} of "$H_2SO_4 \cdot 3H_2O$" Crystals

0°C. = 273.16°K.

$T_{av.}$, °K.	ΔT, approx.	C_p	$T_{av.}$, °K.	ΔT, approx.	C_p
	Series 1		170.35	8.1	30.43
15.32	1.4	1.27	178.93	8.5	31.77
17.41	2.4	1.78	187.47	8.3	33.20
19.52	2.2	2.31	195.68	8.1	34.62
22.57	2.3	3.11	204.61	9.0	35.73[a]
25.76	3.6	3.96	212.83	7.7	38.85[a]
29.23	3.3	4.80	222.84	7.6	38.20
30.87	3.3	5.30	229.45	5.7	59.63
34.98	4.8	6.41	232.96	2.0	57.82
39.83	4.7	7.71			
44.56	4.6	8.91		Series 2	
49.34	4.9	10.01	176.23	8.1	31.13
54.24	4.8	11.20	184.61	8.4	32.46
58.78	4.3	12.24	193.08	8.7	33.83
62.98	4.3	13.23	204.95	11.8	35.48
67.12	3.9	14.07	215.49	8.9	37.67
71.18	4.2	14.91	224.29	9.0	39.50
75.39	4.3	15.73	229.19	2.5	41.57
80.93	6.9	16.71	232.71	2.5	42.08
87.57	6.4	17.87	235.09	2.2	49.95
94.10	6.8	18.91			
100.70	6.4	19.97		Series 3	
107.20	6.6	20.97	197.49	7.4	34.33
114.14	7.3	21.99	203.32	6.1	35.17
121.16	6.6	23.03	210.26	7.6	36.06
127.83	6.7	24.08	217.95	7.6	39.09
134.64	7.1	25.01	224.82	6.1	39.14
142.10	7.6	26.03	229.05	2.4	40.52
149.70	7.6	27.26	231.69	3.0	42.14
157.67	8.2	28.32	234.52	2.6	49.92
166.02	8.6	29.60			

[a] Resistance thermometer temporarily strained. Run calculated from thermocouple measurements.

When several different crystalline substances are forming simultaneously, the one closest to the composition of the liquid would be expected to have the highest rate of crystallization. Barring some highly specific factors, the necessity of displacing the components, particularly in viscous liquids, will reduce the chance of forming much of the off composition phases. This reasonable surmise corresponds with the facts of the present case.

The measured heat absorbed at the eutectics served not only to indicate the presence of the phases but allowed the quantitative evaluation of the amounts present. For making these calculations we had the data of Rubin and Giauque[2] on the mono-, di- and tetrahydrates. The data on the tetrahydrate, which were not included in the above reference due to small errors, caused by the presence of non-equilibrium phases, were more accurate than necessary for the small correction involved here.

Data of Kunzler and Giauque[7] on the partial molal heat contents, heat capacities, and the temperature coefficients of the latter in the liquid range below room temperature were also available. These data permitted the calculation of the heat of fusion at any of the eutectics concerned.

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(6) C. M. Gable, H. F. Betz and S. H. Maron, This Journal, **72**, 1445 (1950).

(7) J. E. Kunzler and W. F. Giauque, data to be published.

Comparison of heat capacity results of Series 1 with those of Series 2 and 3, to be mentioned below, showed that there was a small amount of material in Series 1 which did not crystallize. This could be detected only in the region where the heat capacity of the super-cooled liquid is more than twice that of the crystalline material. An additional indication of the presence of a small amount of uncrystallized material was the evolution of a small amount of heat near 217°K. between measurements in Series 1. Due to simultaneous but unrelated experimental difficulties, at this time, the heat could not be accurately evaluated. It is not surprising that a small amount of material supercools since chance is involved in the appearance of the monohydrate needed to form the monotetrahydrate eutectic. There is no reason to expect that all of the several small regions, in which the liquid is undoubtedly trapped, would produce the necessary monohydrate crystals. The final composition of the glass when it "solidified," some 40 to 50° below the monotetra eutectic temperature, should have been approximately that of the dihydrate. By analogy with the trihydrate glass the small amount of uncrystallized material was estimated at 0.25 mole %. Since glasses and crystals have almost the same heat capacities in the solid region of the supercooled liquid, the presence of the non-crystalline material could hardly have affected the heat capacity below 150°K. by more than 0.02%. At higher temperatures the course of the heat capacity curve was determined by Series 2 and 3, Table II, where there was no evidence of any uncrystallized material. The mole percentages of the several phases present in Series 1 are given in Table III. The values given for Series 1 in the table indicate the amounts of the several phases in the solid at low temperatures. Above about 217°K. the liquid from the glass impurity and also from the monotetra eutectic crystallized to form tri- and dihydrates. It may be shown that these are the only possible phases into which crystallization can occur under these conditions. A heat capacity measurement after the crystallization indicated that essentially all of the material had crystallized.

TABLE III

QUANTITATIVE THERMAL ANALYSIS OF SAMPLES OF "$H_2SO_4 \cdot 3H_2O$"

Substance	Mole per cent. Series 1	Series 2	Series 3
$H_2SO_4 \cdot H_2O$	0.49	0.16	0.21
$H_2SO_4 \cdot 2H_2O$	.61	...	...
Glass	.25	...	...
$H_2SO_4 \cdot 3H_2O$	96.88	99.59	99.44
$H_2SO_4 \cdot 4H_2O$	1.77	0.25	0.35

When various crystalline forms have existed in a calorimeter, followed by melting, the composition cannot remain uniform. During crystallization solids of other than trihydrate will force liquid of the remaining composition to some other location. During melting, various hydrates will tend to sink or float with consequent dislocation of the components. In order to re-establish uniformity, after complete melting, the liquid was stirred by convection associated with heat input. This can be made more effective by applying the heat to the lower part of the calorimeter as can be done by means of the sectionalized resistance thermometer-heaters of the condensed gas or liquid type calorimeters used in this Laboratory.

In a successful attempt to increase the amount of the material crystallizing as trihydrate the following procedure was used.

The liquid was supercooled about 50° below the transition temperature and the calorimeter was held in a high vacuum until crystallization started. Helium was then admitted to the insulating vacuum space so that the heat of crystallization would be largely removed by heat transfer to colder surroundings. This prevented the calorimeter from warming to the transition temperature. Series 2 and 3 of Table II were obtained on material prepared in this way. In the case of Series 3, the insulating space was evacuated and the calorimeter was reheated almost to the transition point. It was then cooled slowly to about 56° below the transition over a period of two days.

The results of the quantitative thermal analyses for Series 2 and 3 are also given in Table III. In Series 2 and 3 only the monotrihydrate eutectic appeared. If the composition had been exactly that of the trihydrate, it is probable that a large number of attempts would include one in which only trihydrate crystallized; however, there is no reason to believe that the accuracy of the work would be greatly improved by attaining this ideal.

The crystallization of substances from supercooled liquids is rather rough treatment for a calorimeter because the space becomes filled with phases which are contracted below the volumes characteristic of their melting points. Subsequent heating can cause expansion which will strain the calorimeter. In the present case the melting at the eutectic temperatures and along the equilibrium curves above the eutectic temperatures did much to alleviate strain. Had such strains not caused a defect to develop in the resistance thermometer an additional series to cover the range of Series 1 with a higher percentage of trihydrate would have been measured. However, there would seem to be little if anything to be gained by additional measurements.

Corrections for the heat capacities of the amounts of mono-, di- and tetrahydrates present were made on the basis of data available from the work of Rubin and Giauque.[2] These corrections were mostly of the order of 0.1% since the effects of matching higher and lower hydrates largely balanced. This balancing also means that any error in determining the amounts of the several phases present will have a trivial effect on the final results. The observations on the crystals in Table II do not include these small corrections; however, they were incorporated in smoothed values used to evaluate the entropy. The smoothed values will be published later[8] as part of a thermodynamic treatment of the H_2SO_4–H_2O system.

The heat capacity data are plotted in Fig. 1

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(8) W. F. Giauque, J. E. Kunzler and T. R. Rubin, data to be published.

which serves to compare the data for the supercooled liquid and crystals. The results are very similar to those obtained by Gibson and Giauque[5] for glycerine glass and crystals. In Fig. 1 the irregular points below the melting point are due to heat absorbed at eutectic temperatures and premelting effects along temperature-composition curves.

The Heat of Fusion.—The heat of fusion at the transition temperature 236.72°K. was measured by melting each of the samples referred to as Series 2 and 3 in Tables II and III. The values found were 5779 and 5784, average 5782 ± 10 cal. mole^{-1}. In each case the result was corrected for the premelting heat which had been absorbed up to the initial temperature and for the presence of the other hydrates. An approximate value of the heat of fusion, 5774 cal. mole^{-1}, was obtained after Series 1; however that case was so complicated that this value was given no weight.

The Entropy of Supercooled and Crystalline $H_2SO_4 \cdot 3H_2O$.—The entropy calculations are summarized in Table IV.

TABLE IV

ENTROPY, IN CAL. DEG.$^{-1}$ MOLE^{-1}, CALCULATIONS FOR GLASS AND CRYSTALS OF $H_2SO_4 \cdot 3H_2O$

Glass and liquid	
0–15°K., extrapolation	0.49
15–298.16°K. $\int C_p \, d \ln T$	76.54
$S_{298.16} - S_{0°K.}$	77.0
Crystals and liquid	
0–15°K., extrapolation	0.42
15–236.82°K. $C_p \, d \ln T$	40.744
Fusion, 5786/236.82	24.432
236.82–298.16°K. $\int C_p \, d \ln T$	17.301
$S_{298.16}$	82.90 ± 0.1

In making the calculation of the entropy change in the glass the 26 cal. mole^{-1} evolved during annealing near 152°K. was ignored. This temperature is just before the rapid rise in heat capacity and had the measurements been taken rapidly the entropy change in the glass would have been about 0.16 cal. deg.$^{-1}$ mole^{-1} less. This means that the less annealed glass retained somewhat more disorder and a corresponding higher entropy near 0°K. Since the glass and crystals differ little in heat capacity one would hardly expect much difference between annealed and unannealed glass except in the softening region. In making the entropy calculation the melting point was estimated as 0.1° above the transition temperature 236.72°K. The heat of fusion at the unstable melting point, 236.82 becomes 5786 cal. mole^{-1} when a correction of 4 calories is added for the change over the 0.1° interval.

It will be shown in a later paper[8] that the trihydrate, as well as the mono- and dihydrates and anhydrous H_2SO_4 all approach zero entropy at the absolute zero of temperature. Thus the value 82.90 cal. deg.$^{-1}$ mole^{-1} is the value which should be used in ordinary thermodynamic calculations. It does not include the effects of nuclear spin or isotopes which cancel in ordinary reactions.

The glass retains a considerable amount of disorder at 0°K. corresponding to 5.9 cal. deg.$^{-1}$ mole^{-1} of entropy. The results provide another example of the fact that a supercooled liquid cannot be used to obtain the absolute entropy by means of the third law of thermodynamics.

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The Heat Capacities and Entropies of Sulfuric Acid and Its Mono- and Dihydrates from 15 to 300°K.[1]

BY T. R. RUBIN AND W. F. GIAUQUE

The heat capacities of sulfuric acid and its mono- and dihydrates have been measured from 15 to 300°K. The melting points were found to be 283.53, 281.64 and 233.69 ± 0.05°K., respectively. The heats of fusion at the melting points are 2560, 4646 and 4360 cal. mole^{-1}, respectively. The entropies as calculated by means of the third law of thermodynamics were found to be 37.49, 50.49 and 66.14 cal. deg.$^{-1}$ mole^{-1}, respectively, at 298.16°K. It will be shown in a later publication that there is no residual entropy due to random hydrogen bonds or other type of disorder. Thus the above values may be used in ordinary thermodynamic calculations.

The investigation reported here was undertaken to extend and improve the thermodynamic data relating to sulfuric acid and its aqueous solutions. We were especially interested in securing data which will add to our understanding of possible residual entropy due to disordered hydrogen bonding at low temperatures. The detailed crystal structures of sulfuric acid and its hydrates are not yet known, so it was not possible to find a basis for predicting whether such false equilibrium may complicate the application of the third law of thermodynamics, as in the case of ice.[2a,b]

All of the calorimetric measurements were made with an apparatus that has been described previously[3] as Gold Calorimeter III. The calorimeter is one of those used in this Laboratory for condensed gases which can be distilled in and out through a long glass tube. In the present case the sulfuric acid was introduced and removed by means of a long, small diameter, gold tube which could be inserted in

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(1) The experimental work reported here was completed in 1940. Final calculations have been made with assistance provided by the Office of Naval Research, United States Navy.

(2) (a) L. Pauling, THIS JOURNAL, **57**, 2680 (1935); (b) W. F. Giauque and W. J. Stout, *ibid.*, **58**, 1144 (1936).

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