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The Low Temperature Heat Capacity and Entropy of Sulfuric Acid Hemihexahydrate. Some Observations on Sulfuric Acid "Octahydrate"[1]

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Sulfuric acid has been shown, both by chemical and thermodynamic analysis, to have a hemihexahydrate, $H_2SO_4 \cdot 6.5H_2O$. Previous investigators have reported this substance as the "hexahydrate." The heat capacity of $H_2SO_4 \cdot 6.5H_2O$ has been determined from 15 to 320°K. The ice-hemihexahydrate eutectic temperature is 211.28°K. The peritectic between $H_2SO_4 \cdot 4H_2O$, $H_2SO_4 \cdot 6.5H_2O$ and equilibrium solution occurs at 219.53°K. The unstable melting point of the hemihexahydrate was observed directly as 220.28°K., and the heat of fusion at this temperature was found to be 8162 cal. mole^{-1}. The calorimetric problem of measuring the heat of fusion of a substance which decomposes at a peritectic temperature is discussed. The $\int_0^{298.16°\text{K.}} Cp \, d \ln T$ of $H_2SO_4 \cdot 6.5H_2O$ was found to be 140.61 cal. deg.$^{-1}$ mole^{-1} at 298.16°K. The entropy was also calculated from data on the reaction, $H_2SO_4 + 6.5H_2O(l) = H_2SO_4 \cdot 6.5H_2O$; $S(H_2SO_4 \cdot 6.5H_2O) = S(H_2SO_4) + 6.5\ S(H_2O) + (\Delta H - \Delta F)/T = 140.51$ cal. deg.$^{-1}$ mole^{-1} at 298.16°K., in excellent agreement with the above value. Hulzmann and Biltz interpreted the lower of two fixed points in the aqueous sulfuric acid system as the eutectic between ice and "octahydrate," the upper as the "octahydrate"-"hexahydrate" peritectic. Gable, Betz and Maron reinterpreted the data in terms of other known phases and decided there was no evidence for "octahydrate." The present work shows that the "lower fixed point" is actually two fixed points 0.43° apart. These are interpreted as the ice-"octahydrate" eutectic at 200.60°K. and a peritectic between "octahydrate," tetrahydrate and equilibrium solution at 201.03°K. The point interpreted as the "octahydrate"-"hexahydrate" peritectic by Hulzmann and Biltz is actually the ice-hemihexahydrate eutectic mentioned above. No one has ever analyzed a solid phase of composition $H_2SO_4 \cdot 8H_2O$. Attempts to obtain this pure phase for analysis were unsuccessful, nor could it be cooled to low temperatures without inducing spontaneous transformation. The best evidence that the solid phase is "sulfuric acid octahydrate" is that the melting curve, extrapolated into the unstable region above the peritectic, appears to have zero slope near that composition.

This paper is a continuation of a series of investigations on the thermodynamics of the sulfuric acid water system including low temperature data on the several hydrates. It contains observations on the last two of the known hydrates of sulfuric acid. These had been reported[2] to be the "hexa-" and "octahydrates." However after material of the composition $H_2SO_4 \cdot 6H_2O$ was investigated calorimetrically it was necessary to conclude that the "hexahydrate" did not appear as a solid phase and that 80% of the acid crystallized as hemi-hexahydrate, $H_2SO_4 \cdot 6.5H_2O$, and 20% as tetrahydrate. That this was the case was confirmed by later experiments.

When material of the composition $H_2SO_4 \cdot 8H_2O$ was placed in the calorimeter we did not succeed in cooling the "octahydrate" to low temperatures. It was however possible to observe two fixed points, which we identify as the ice-"octahydrate" eutectic, and the peritectic between "octahydrate," tetrahydrate, and the equilibrium liquid.

Apparatus and Preparation of the Samples.—The calorimeter has been described previously[3] in connection with measurements on the tri- and tetrahydrates. The defined calorie was taken as 4.1840 absolute joules. In order to retain consistency with all of the previous papers of the series on aqueous sulfuric acid, 0°C. was taken equal to 273.16°K. Correction to the value 0°C. = 273.15°K. recently adopted by international agreement will be made in a final paper which will correlate and summarize all of the data on the H_2SO_4-H_2O system.

The samples were prepared from Baker and Adamson C.P. sulfuric acid which was redistilled and diluted with distilled water. It was analyzed by weight titration against 6 *N* NaOH. Constant boiling sulfuric acid was used as a reference standard as described by Kunzler.[4]

Crystallization of Material with the Over-all Composition $H_2SO_4 \cdot 6H_2O$.—Aqueous sulfuric acid is practically certain to supercool before crystallization occurs. When a substance has a peritectic point one procedure is to supercool the calorimeter well below the peritectic temperature and hope that the phase corresponding to the selected composition will crystallize. After crystallization starts it is likely to be slow enough so that heat can be removed from the calorimeter at a rate which will prevent it from heating to the peritectic temperature.

Numerous experiments led us to the conclusion that the tetrahydrate is likely to appear spontaneously even from solutions which are considerably off that composition. This caused great difficulty in our experiments with the hemihexahydrate.

Since the statements of previous workers led us to expect the appearance of the "hexahydrate," material of the composition $H_2SO_4 \cdot 6.0034H_2O$ was placed in the calorimeter. After crystallization it was found that about 0.1 mole of ice per mole of H_2SO_4 appeared at 211.2°K., which had been reported[5] (211.18°K.) as the ice-"hexahydrate" eutectic temperature. Subsequent warming, to the peritectic point, without much loss of hemihexahydrate, followed by cooling, essentially removed the ice. This is not surprising since it was finally determined that some 20% of the solid was in the form of tetra- and 80% hemihexahydrate to balance the over-all composition of $H_2SO_4 \cdot 6H_2O$. The large excess of tetra made it relatively easy for the ice to combine with it to produce $H_2SO_4 \cdot 6.5H_2O$.

There was however no way in which the observations at this point could tell us that the calorimeter did not contain essentially pure "hexahydrate." The low temperature heat capacities and heat of fusion were measured on this material. Calculations made later showed thermodynamic inconsist-

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(1) This work was supported in part by the National Science Foundation, and by the Office of Naval Research, United States Navy. It may be reproduced or used in any way by the United States Government.

(2) O. Hulzmann and W. Biltz, *Z. anorg. allgem. Chem.*, **218**, 369 (1934).

(3) E. W. Hornung and W. F. Giauque, THIS JOURNAL, **77**, 2983 (1955).

(4) J. E. Kunzler, *Anal. Chem.*, **25**, 93 (1953).

(5) C. M. Gable, H. F. Betz and S. H. Maron, THIS JOURNAL, **72**, 1445 (1950).

encies that led to the discovery that the calorimeter actually contained hemihexa- and tetrahydrate.

Proof that a Solid of Composition $H_2SO_4 \cdot 6.5H_2O$ Crystallizes from Aqueous Sulfuric Acid.—The measurement of the heat of fusion of a substance which undergoes a transition at a peritectic presents a number of complications which will be discussed in detail below. Since the heat of fusion is calculated to correspond to the unstable melting point above the peritectic temperature, it is necessary that the melting point be determined. As long as material of composition $H_2SO_3 \cdot 6H_2O$ was in the calorimeter it was not possible to superheat crystals of the hemihexahydrate for a direct melting point observation.

It was decided to use the various partial molal properties available from the present series of measurements[6] on aqueous sulfuric acid to calculate the melting point. This made use of the peritectic temperature and composition as a starting place and the ice-hydrate eutectic as a check. When this was done the ice-"hexahydrate" eutectic did not agree as is shown in Fig. 1.

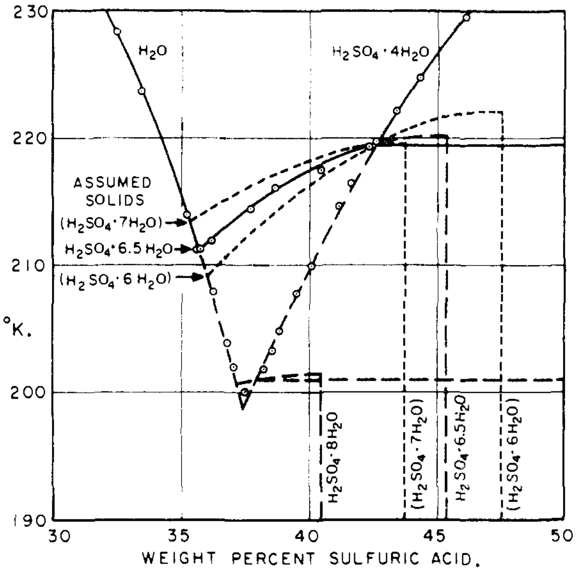

Fig. 1.—Calculated freezing point curves: ⊙, Gable, Betz and Maron; ——, stable; — — —, unstable; - - -, hypothetical.

Various suppositions were then made as to what the composition of the hydrate might be. For example a calculation assuming heptahydrate is shown in Fig. 1. In such a calculation the heat of fusion is reinterpreted to allow for the amount of tetrahydrate which must be present to be consistent with the over-all composition $H_2SO_4 \cdot 6H_2O$.

The above procedure indicated that the composition of the principal solid phase had to be $H_2SO_4 \cdot 6.5H_2O$ as is also shown in Fig. 1. The melting curve data of Gable, Betz and Maron[5] also fall well on the curve calculated for $H_2SO_4 \cdot 6.5H_2O$.

In the initial calculation of the freezing point curve of the hemihexahydrate the peritectic temperature was taken as our measured value 219.53°K. and the composition of the equilibrium liquid was taken from the freezing point curve of the tetrahydrate as measured by Gable, Betz and Maron.[5] This corresponds to $A = 7.33$ moles of water per mole of sulfuric acid. This gave a calculated melting point for the hemihexahydrate of 220.33°K. against the reliable value determined later as 220.28°K.

The final calculations, which were based on the observed melting point 220.28°, gave 219.5°K. for the peritectic, against 219.53°K. observed, with the calculated composition at $A = 7.29$ moles H_2O/mole H_2SO_4 for the equilibrium liquid at the peritectic. The ice-hemihexahydrate eutectic temperature was calculated to be 211.2°K., compared to 211.28°K. observed, with an $A = 9.78$ for the eutectic composition. These values were obtained from the intersection of the calculated freezing point curves.

To confirm the above result a number of "test-tube" experiments were performed. Liquid of the composition $H_2SO_4 \cdot 6.5H_2O$ was supercooled a little, by surrounding it with similar material at the peritectic temperature. According to the new interpretation, material with a composition near $H_2SO_4 \cdot 8H_2O$ should be stable only with respect to the solid $H_2SO_4 \cdot 6.5H_2O$ along its freezing curve between the ice–hemihexa eutectic and peritectic temperatures, as is indicated in Fig. 1. Some seeds of a solid obtained from material in this composition region were added to the supercooled $H_2SO_4 \cdot 6.5H_2O$ solution. In a subsequent 16-hour period several clear crystals, about 5 mm. across, were formed. These were lifted out of the liquid and drainage from a small amount of melting was permitted to eliminate the solution which adhered to them. They were then analyzed and found to have the composition $H_2SO_3 \cdot 6.502H_2O$ which corresponded to 6.500 within the limit of error of this experiment. The solution from which the crystals formed was also analyzed and found to be $H_2SO_3 \cdot 6.535H_2O$ due to the addition of the more dilute solution containing seeds.

Before the above crystals were removed for analysis the tube containing them was placed in another Dewar vessel and allowed to come to equilibrium at their melting point. By means of a copper–constantan thermocouple the melting point was found to be 220.27°K., which agrees well with our later determination, 220.28°K. The peritectic temperature, 219.53°K., was used as a comparison reference between the above thermocouple and the standard thermocouple.

Following this experiment, a solution with the composition $H_2SO_4 \cdot 6.5H_2O$ was placed in the calorimeter. A glass tube about 2 mm. i.d. and 145 cm. long connects the gold calorimeter to a stopcock and line above. Access is so difficult that we had always previously thought that seeding was impracticable. However it was accomplished by the following procedure. A small amount of material which could contain only hemihexahydrate and ice crystals was ground to a fine powder in liquid nitrogen. The seeds were placed in a small cooled bulb above the tube leading to the calorimeter, which was cooled below the melting point of the hemihexa-

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

hydrate, and evacuated. When the stopcock was opened an atmosphere of helium drove some of the finely powdered seed crystals into the calorimeter. Crystallization began at once.

The Unstable Melting Point of Sulfuric Acid Hemihexahydrate.—The crystallization following the above procedure warmed the calorimeter to 220.28°K., which was thus determined to be the unstable melting point of sulfuric acid hemihexahydrate. The substance stayed at the melting point for two hours at which time observations were terminated. By the following day the tetrahydrate had formed and the resultant heat evolution had increased the temperature until all of the hemihexahydrate had transformed. This material was removed from the calorimeter for reasons to be discussed below.

Re-evaluation of the Proof that $H_2SO_4 \cdot 4H_2O$ Crystallizes Accurately at that Composition.—Hornung and Giauque[3] included a section in which they calculated the purity of the solid tetrahydrate phase on the assumption that excess water crystallized as $H_2SO_4 \cdot 6H_2O$. This calculation is invalid since we now know that $H_2SO_4 \cdot 6.5H_2O$ should have been used. Repetition of the calculation, with accurate data for the heat of the peritectic transition, has led us to conclude that the data were misinterpreted. It is believed that the small amount of water added accidentally to the surface of the calorimeter was not completely mixed prior to the observation used for this calculation. Had this been realized a heat effect would have been sought on the acid as well as on the water side of the tetrahydrate. This was not done. However, the later data given in their Table I were obtained after some water had been pumped off and the sample had been heated to ordinary temperatures to ensure mixing. These results show that eutectic melting and premelting agreed with each other and with the titration analysis to 0.006% on the assumption that $H_2SO_4 \cdot 4H_2O$ was the solid phase. Accordingly we reach the conclusion that the tetrahydrate crystallizes as a pure compound $H_2SO_4 \cdot (4.0000 \pm 0.0005)$ instead of the previous value (4.0000 ± 0.0001) based on what we formerly assumed to be superior data.

Sulfuric Acid "Octahydrate."—On the basis of warming curves for aqueous sulfuric acid, Hulzmann and Biltz[2] found fixed points at 200.8 and 211°K., which they interpreted as the ice–"octahydrate" eutectic, and the "octahydrate"–"hexahydrate" peritectic.

Gable, Betz and Maron[5] found essentially the same fixed points at 200.06 and 211.18°K. They interpreted the lower point as the ice–tetrahydrate eutectic and the upper point as the ice–"hexahydrate" eutectic and decided that their work contained no evidence for the existence of an "octahydrate."

The present work shows that the upper temperature, which we found to be 211.28°K., is due to the ice–hemihexahydrate eutectic. However, we found two fixed points near the lower value which had been given by Hulzmann and Biltz, and by Gable, Betz and Maron. These are 200.60 and 201.03°K.

Calculations based on our tables of the thermodynamic properties of aqueous sulfuric acid show that the eutectic temperature for the ice–tetrahydrate should be approximately 198.6°K. with $A = 9.09$. These values are somewhat more uncertain than those at higher temperatures due to the considerable extrapolation of the partial molal properties. This eutectic was not observed and it is probable that the ice combined with tetrahydrate to form hemihexahydrate in our experiments.

This leads us to conclude that the fixed point at 200.60°K. corresponds to a eutectic between ice and another hydrate. It seems plausible that it is the "octahydrate" and that the observed temperature at 201.03°K. is the peritectic temperature between the "octahydrate," tetrahydrate and equilibrium solution. The reason why tetrahydrate was selected as an equilibrium phase is that the temperature 201.03°K. was obtained in experiments with various solutions such as $H_2SO_4 \cdot 6H_2O$, $H_2SO_4 \cdot 6.5H_2O$ and $H_2SO_4 \cdot 8H_2O$ under circumstances where the tetrahydrate could be shown to be present. When such mixtures are cooled the tetrahydrate nearly always crystallizes as may be shown by the fact that the heat of crystallization causes the temperature to rise to the freezing point curve of the tetrahydrate. This increases the water content of the remaining solution and makes it possible for "octahydrate" to crystallize. Any excess water becomes ice at the ice–"octahydrate" eutectic.

All attempts to obtain reasonably pure "octahydrate" from a solution of composition $H_2SO_4 \cdot 8H_2O$ failed because tetrahydrate appeared. When a mixture containing considerable "octahydrate" along with tetrahydrate and some ice was cooled to about 195°K. a transformation was initiated with the evolution of heat. Warming continued until temperatures above the stability range of the "octahydrate" were reached. Subsequently it could be shown that hemihexahydrate was present through observation of the ice–hemihexahydrate eutectic temperature.

The free energy data at 25° combined with the various partial molal quantities were used to calculate the composition at the ice–"octahydrate" eutectic as $A = 9.20$. A similar calculation for the "octahydrate"–tetrahydrate peritectic gave the composition of the equilibrium liquid as $A = 8.88$.

The Calorimetric Problem Involved in Measuring the Heat of Fusion of a Substance with an Unstable Melting Point.—When a substance has an unstable melting point there is always a chance that it may melt normally to its supercooled liquid during a determination of the heat of fusion. This was not found to be possible in the present experiments with $H_2SO_4 \cdot 6.5H_2O$ since the stable tetrahydrate and the equilibrium liquid always appeared at the peritectic temperature shown in Fig. 1. The tetrahydrate has a greater density than the liquid and thus sinks to the bottom where it melts as the temperature and composition rise along the tetrahydrate melting curve. At the end of the process the composition at the bottom will be considerably more concentrated than the average while that at the top will be near that of the equilibrium liquid at the peritectic point. At intermediate levels the concentration will vary according to somewhat accidental circumstances, concerned with the shape of the calorimeter, the rate of heating and opportunity for convection.

When aqueous sulfuric acid of two differing concentrations is mixed, heat is always evolved and if the dislocation of acid and water described above is ignored, it is evident that the apparent heat of fusion will be too high.

Several values of the heat of fusion of the hemihexahydrate were obtained by different methods. Two values were calculable from heat input during series of measurements made when the over-all composition was $H_2SO_4 \cdot 6H_2O$, when we were under the illusion that this was the solid phase. When it was found that the solid consisted of a mixture of hemihexa- and tetrahydrates the result could be corrected for the amount of tetrahydrate present. The heat of fusion of tetrahydrate has been reported previously.[3] The problem of concentration dislocation was solved by measuring the heat content over the whole temperature range to 25°. During this lengthy procedure convection produced mixing. By calculation the solution could then be considered as fractions of tetra- and hemihexahydrates of known heat content and their respective $\int C_p\,dT$'s subtracted. This mixing procedure was used only on one of these two measurements and it was assumed to be the same on the other one. Stirring would have been a better way to assure uniform mixing but the use of a stirrer was impracticable.

Another procedure was tried on a second sample of composition $H_2SO_4 \cdot 6.501H_2O$ which was placed in the calorimeter and seeded so as to produce essentially pure hemihexahydrate. This substance decomposed during fusion and heat was added until the last of the resulting tetrahydrate was melted. A long gold tube with an i.d. of about 1 mm. was then lowered to the bottom of the calorimeter and the contents were removed in 12 portions of about 10 cc. each. The material was removed over a period of about 50 minutes and it was hoped that the liquid would sink uniformly as the denser portions were removed at the bottom. This would require essentially horizontal flow along the bottom of the calorimeter to the gold tube at the center. Despite the very slow rate of flow it is doubtful that the rather viscous liquid would quite attain this ideal mechanism of flow. The temperature of the calorimeter was observed during the removal of the liquid and the absence of appreciable heat effect indicated trivial mixing within the calorimeter during this process. This does not prove that the portions withdrawn supply a completely correct account of the concentration as a function of level in the liquid as any form of streamline flow should not involve much mixing within the calorimeter. A smoothed curve through the results gave values of $A = 5.02$, 5.78, 6.16, 6.36, 6.48, 6.58, 6.68, 6.81, 6.95, 7.04 and 7.10 for the values 0, 0.1, 0.2, ..., 1.0 mole of H_2SO_4 where A represents moles of H_2O/mole H_2SO_4. Since all heat quantities of the liquid solutions are known,[6] correction was made for the heat of mixing. This was found to be 11.5 cal. mole^{-1}.

The results of the two methods of determining the heat of fusion are given in Table I.

A fourth measurement of the heat of fusion of hemihexahydrate was obtained during our attempts to cool the "octahydrate." Liquid of this over-all composition crystallized as hemihexahydrate plus some ice as a eutectic mixture. It was decided that at the conclusion of the eutectic melting, the eutectic liquid was held in the interspaces between the hemihexahydrate crystals. This situation should somewhat minimize concentration dislocation due to subsequent melting. Also the more dilute solution should correspond to less heat effect. Since the mixing correction in method II was only 11.5 cal. mole^{-1} it is doubtful if the correction in this case would amount to more than several cal. mole^{-1}. Thus no mixing correction was applied.

TABLE I

HEAT OF FUSION OF SULFURIC ACID HEMIHEXAHYDRATE AT ITS UNSTABLE MELTING POINT, CAL. DEG.$^{-1}$ MOLE^{-1}

M.p. 220.28°K., 0°C. = 273.16°K.

Method I	ΔF Fusion
Substance melted	$H_2SO_4 \cdot 6.5H_2O$
0.5744 mole $H_2SO_4 \cdot 6.5H_2O$	
.1424 mole $H_2SO_4 \cdot 4H_2O$	
Measurement 1	8157
Measurement 2	8164
Method II	
Substance melted	
0.7769 mole $H_2SO_4 \cdot 6.5H_2O$	8169
.0008 mole H_2O	
Method III	
Substance melted	
0.6167 mole $H_2SO_4 \cdot 6.5H_2O$	
.9257 mole H_2O	8160
Accepted value	8162

The first method above is handicapped by the fact that a heat capacity correction involving an amount 125% of the heat of fusion was necessary. Any error in the mixing correction of any of the above methods should lead to high values of the heat of fusion. However, the general agreement indicates little error due to this effect.

The Heat Capacity of Sulfuric Acid Hemihexahydrate.—The heat capacity of $H_2SO_4 \cdot 6.5H_2O$ may be obtained from measurements on the sample with the over-all composition $H_2SO_4 \cdot 6.0034H_2O$. Since our work with the various hydrates of sulfuric acid has led us to believe that no solid solutions are formed in the case of any of these hydrates the results were corrected for the 19.864 mole % of tetrahydrate present. The heat capacity of $H_2SO_4 \cdot 4H_2O$ was available from the work of Hornung and Giauque.[3]

Several low temperature measurements were made on the pure $H_2SO_4 \cdot 6.5H_2O$ prior to the heat of fusion determination. They agreed within the limit of error with those obtained from the mixture. The fact that the hemihexahydrate had been crystallized from a supercooled solution caused considerable stretching of the calorimeter and its resistance thermometer. It was necessary to calculate these results by means of the thermocouple observations. Since this gave a somewhat reduced accuracy these results were given no weight and are not tabulated. The observations on the solid mixture of hemihexa- and tetrahydrate are given in Table II. The heat capacity of the hemihexahydrate, after correction for the tetrahydrate present, is not given here, since this will be included in a summarizing paper with smoothed tables for all of the hydrates.

TABLE II

HEAT CAPACITY OF $H_2SO_4 \cdot 6.0034H_2O$, CAL. DEG.$^{-1}$ MOLE^{-1}

0°C. = 273.16°K.

0.57444 mole $H_2SO_4 \cdot 6.5H_2O$ } in the
0.14239 mole $H_2SO_4 \cdot 4H_2O$ } calorimeter

T, °K.	ΔT	Cp	T, °K.	ΔT	Cp
14.77	2.06	1.93	101.14	7.01	31.11
17.28	2.38	3.02	108.18	7.07	32.79
19.85	2.48	3.88	115.17	6.81	34.45
21.15	3.18	5.13	122.26	7.17	36.03
24.25	3.50	6.60	129.56	7.27	37.68
27.73	3.99	8.24	136.66	6.94	39.28
34.10	4.73	10.09	143.75	7.07	40.91
36.42	4.40	11.97	151.12	7.44	42.59
48.77	6.38	15.81	158.41	7.00	44.25
54.97	6.08	18.08	165.30	6.63	45.84
60.92	5.75	20.20	172.16	6.92	47.42
66.89	6.19	22.17	179.34	7.17	49.07
73.28	6.57	24.25	186.57	6.80	50.75
80.06	6.93	26.15	193.02	5.81	52.27
86.95	6.85	27.77	205.18	5.83	55.23
94.01	7.30	29.38	211.29	6.05	58.51
			216.63	4.59	61.23

TABLE III

HEAT CAPACITY OF LIQUIDS WITH THE COMPOSITIONS $H_2SO_4 \cdot 6H_2O$, $H_2SO_4 \cdot 6.5H_2O$ AND $H_2SO_4 \cdot 8H_2O$, CAL. DEG.$^{-1}$ MOLE^{-1}

0°C. = 273.16°K.

$H_2SO_4 \cdot 6.003H_2O$		$H_2SO_4 \cdot 6.501H_2O$		$H_2SO_4 \cdot 8.001H_2O$	
T, °K.	Cp	T, °K.	Cp	T, °K.	Cp
		Series 1			
213.74	115.84	230.18	126.89	213.17	143.00
221.25	117.54	236.69	128.65	220.82	146.47
229.34	119.29	244.03	130.40	228.81	149.98
237.54	120.74	251.38	131.50	236.71	153.11
245.93	122.22	258.75	133.13	244.52	155.91
254.61	123.60	266.14	133.57	252.60	158.29
263.65	124.75	273.25	134.62	261.08	160.41
272.70	125.76	280.89	135.24	269.90	161.92
281.74	126.33	289.06	135.78	278.67	163.38
290.86	126.85	296.61	136.34	287.19	163.89
299.76	127.04			295.68	164.19
		Series 2			
		295.26	136.09		
		303.00	136.55		
		310.81	136.83		
		318.81	136.99		

The Heat Capacity of the Liquids $H_2SO_4 \cdot 6H_2O$, $H_2SO_4 \cdot 6.5H_2O$ **and** $H_2SO_4 \cdot 8H_2O$.—During the course of the work results were obtained on liquids of the compositions $A = 6$, 6.5 and 8 moles of water per mole of H_2SO_4. These taken with the earlier results[3,7,8] on other hydrates are of considerable interest in determining the temperature coefficients of the partial molal heat capacities in the temperature range below 25°. The results for $A = 6$, 6.5 and 8 are given in Table III.

The Entropy of $H_2SO_4 \cdot 6.5H_2O$.—The entropy calculation for sulfuric acid hemihexahydrate is summarized in Table IV.

TABLE IV

ENTROPY OF $H_2SO_4 \cdot 6.5H_2O$, CAL. DEG.$^{-1}$ MOLE^{-1}

0–15°K., Debye extrapolation	0.72
15-220.28°K., $\int C_p \, d \ln T$	62.97
Fusion, 8162/220.28	37.05
220.28–298.16°K. $\int C_p \, d \ln T$	39.87
	140.61

This value may be compared with one calculated at 25° from the various thermodynamic properties of aqueous sulfuric acid which will be summarized in a later paper.[6]

$$H_2SO_4 + 6.5H_2O(l) = H_2SO_4 \cdot 6.5H_2O$$

$$\Delta S = \frac{\Delta H - \Delta F}{T} = \frac{-14669 + 12998}{298.16}$$

$$= -5.60 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$H_2SO_4(l),\ S_{298.16} = 37.49 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$H_2O(l),\ S_{298.16} = 16.71 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

From these values the entropy of sulfuric acid hemihexahydrate may be calculated as

$$S(H_2SO_4 \cdot 6.5H_2O) = \Delta S + S(H_2SO_4) + 6.5\ S(H_2O)$$

$$= -5.60 + 37.49 + 108.62$$

$$= 140.51 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

The excellent agreement with the value 140.61, given in Table IV, shows that sulfuric acid hemihexahydrate like the anhydrous acid and its mono-, di-, tri- and tetrahydrates has no residual entropy due to hydrogen bond or other type of disorder at low temperatures.

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

(8) J. E. Kunzler and W. F. Giauque, *ibid.*, **74**, 797 (1952).