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.

We thank Dr. D. W. Osborne for providing careful calibration data on the resistance thermometer on the calorimeter, which he had used previously, and Dr. D. N. Lyon for assistance with the measurements.

Berkeley, California Received July 13, 1951

[Contribution from the Chemical Laboratory of the University of California]

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).

the glass tube. Most of the acid could be withdrawn into a weighing flask. Small amounts which adhered to the walls of the calorimeter were removed by washing with water through the gold tube and evaluated by analysis.

Two minor changes were made in the calorimeter. The glass tube shown at position 3 in Fig. 1 of reference 3 became loose in the Woods' metal support at position 44. This was caused by a slight taper in the tube. A section of the tube was replaced by one with the larger end of a slight taper above rather than below the Woods' metal support. It was found necessary to compensate for unequal tube contraction by means of bellows tubing at position 4 of Fig. 1 of reference 3. Such strain is usually relieved by bowing of the long small diameter glass tube during cooling.

The calibrated thermocouple, of laboratory designation W-25, was found to check the boiling point, 20.36°K., and triple point, 13.92°K., of hydrogen to 0.05°K. 0°C. is taken as 273.16°K. One defined calorie was taken as 4.1833 international joules.

Preparation of Sulfuric Acid and Its Hydrates.—Anhydrous sulfuric acid was approximated by mixing reagent "fuming" sulfuric acid containing 15% SO_3 with "concentrated" reagent 95% acid; the amounts necessary being determined by analyzing both of these to 0.2%.

The impurity, which could be either $H_2SO_4{\cdot}H_2O$ or $H_2S_2O_7$, was determined in the calorimeter by noting the eutectic which appeared. Its amount was estimated from a calorimetric measurement of the premelting effect. The amount of acid estimated to be necessary was added following which the eutectic and premelting were again observed. The heat effect at the $H_2S_2O_7$–H_2SO_4 eutectic was spread over a range of about 10 degrees. The heat of fusion of the eutectic could be estimated roughly from available data and indicated that an excess of 0.10 mole per cent. of $H_2S_2O_7$ was present. An estimate of the impurity on the basis of premelting heat superimposed on heat capacity measurements below the melting point indicated that the excess of impurity was 0.06 mole per cent. Since the phase diagram of sulfuric acid in this region is available there is no reason to believe that the non-ideal character of the solution is responsible for the discrepancy which is outside the limit of error.

We believe that the result at the eutectic is correct and that the premelting heat estimate is in error for the following reason. Consider a small region containing eutectic phases. After melting has occurred, and the substance is heated above the eutectic temperature, the small liquid regions will grow at the expense of premelting as the liquid tries to assume the composition in equilibrium with the solid at the particular temperature. Since there can be little convection the impurity will be forced to diffuse from a central location to the melting boundary. If the amount of impurity is very small the region will be small and the attainment of equilibrium should not be difficult. However as the liquid regions become larger and particularly if high viscosity impedes diffusion, as in the case with sulfuric acid, the melting boundary will contain less impurity than the average amount in the liquid. Thus the total premelting will be less than would correspond to equilibrium and the estimate of impurity will be low.

Sulfuric acid monohydrate was made by mixing 95% reagent with distilled water to the correct composition (84%) within 2 or 3%. The mixture was frozen slowly until about one-half was crystalline. After decanting the liquid the solid was crushed and placed on a sintered glass filter. Dry air was passed over the material to force the liquid through the filter. About one-half of the crystals were melted during this procedure. The remaining crystals were melted and the material was put in the calorimeter. It was analyzed as described above; the monohydrate contained excess $H_2SO_4{\cdot}2H_2O$ to the extent of 0.14 mole %.

The dihydrate sample was prepared by diluting a sample of monohydrate which was incorrectly assumed to have retained the same composition as the material investigated above. The trihydrate had not been discovered at the time of these measurements and it was not until it was reported and described recently by Gable, Betz and Maron[4] that we arrived at a complete interpretation of our observations. During the measurements of the heat of fusion approximately 204 calories were absorbed at a temperature which was observed as 230.4°K. This is the di-tri eutectic temperature. In a recent investigation on $H_2SO_4{\cdot}3H_2O$ Kunzler and Giauque[5] have obtained data which enable the determination of the amount of trihydrate present as 1.6 mole per cent. from the above heat of fusion of the eutectic.

Sulfuric acid tetrahydrate was made by diluting reagent quality 95% sulfuric acid with distilled water to a concentration approximating the tetrahydrate. This solution was partially frozen and treated similarly to the monohydrate. It seemed difficult to adjust the initial impurity of about 0.1 or 0.2 mole % by calorimetric titration. Another sample was prepared with a similar result. The heat effect associated with eutectic melting occurred near 200°K., which would indicate that the hexahydrate did not form. Gable, Betz and Maron[4] found that it is easy to supercool the solution to the ice–tetrahydrate eutectic at 200.06°K. As is well known sulfuric acid and its aqueous solutions readily supercool to form glasses. Unexplained heat absorption occurred in a measurement over the interval 233–238°K. and this was not understood until recently, when Gable, Betz and Maron[4] found that the trihydrate (transition to tetra and solution near 237°K.) exists. We suspect that a small amount of trihydrate may have crystallized from the supercooled tetrahydrate. This would leave a water rich portion. When the low temperature heat capacity was measured it became evident that a small amount of glass was present at low temperatures. This finally crystallized near 195°K., presumably to form ice–tetrahydrate eutectic. The complex nature of this behavior defied analysis at the time of the experiment. Since the heat capacity of the material in the various forms does not vary much, fairly good values of the heat capacity of the tetrahydrate could be given. However with the knowledge of the existence of the trihydrate, the work will be repeated in the expectation of preparing a purer sample of tetrahydrate. Accordingly the tetrahydrate results are omitted from this paper.

The temperature regions in which the various glasses crystallize within a few hours were noted as near 275°K. for the anhydrous acid, about 260°K. for the monohydrate, 190°K. for the dihydrate and about 225°K. for the tetrahydrate. These data are very approximate.

Melting Point Data.—The melting point measurements on sulfuric acid and its mono- and dihydrates are given in Table I. The observations were made with various percentages in the liquid

TABLE I

MELTING POINTS OF SULFURIC ACID AND SEVERAL OF ITS HYDRATES

0°C. = 273.16°K

Melted, %	T, °K. resistance thermometer	T, K°. thermocouple
	H_2SO_4	
19	283.39	283.38
44	283.46	283.44
57	283.47	283.47
	Accepted value	283.53 ± 0.01
	$H_2SO_4{\cdot}H_2O$	
19	281.62	281.63
35	281.64	281.64
46	281.64	281.64
60	281.62	281.64
	Accepted value	281.64 ± 0.05
	$H_2SO_4{\cdot}2H_2O$	
4	230.39	230.40[a]
22	232.90	232.92
50	233.61	233.60
65	233.70	233.66
79	233.67	233.68
	Accepted value	233.70 ± 0.05

[a] Di–tri eutectic temperature.

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

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

state. Measurements were not made with more than 70% of the material melted because the attainment of temperature equilibrium throughout the calorimeter is somewhat more difficult when a small amount of the denser solid is all at the bottom of the calorimeter.

Although the melting curve in the region near H_2SO_4 has been investigated with high accuracy,[6] it was not possible to make an accurate correction for the excess $H_2S_2O_7$, because it was evident from the measurements that it was not uniformly distributed in the viscous liquid. Accordingly we have accepted the value 283.53°K. obtained by Gable, Betz and Maron[4] and also more recently in this Laboratory by Kunzler and Giauque.[6]

The mono- and dihydrates are dissociated so much at their melting points that the flat maxima of the melting curves essentially eleminated the type of difficulty present with the anhydrous acid.

In the case of the dihydrate the temperature 230.40°K., with 4% of the heat required for fusion added, is a reliable determination of the $H_2SO_4 \cdot 2H_2O$–$H_2SO_4 \cdot 3H_2O$ eutectic temperature.

TABLE II

HEAT CAPACITY OF H_2SO_4 IN CAL. DEG.$^{-1}$ MOLE^{-1}

T, °K	ΔT	C_p	T, °K	ΔT	C_p
	Series 1		181.42	6.75	16.35
16.11	1.77	0.93	188.28	7.02	16.85
18.91	2.82	1.47	195.15	6.72	17.27
22.28	3.45	2.07	201.72	6.43	17.74
25.34	2.62	2.61	207.87	7.25	18.14
27.52	2.22	3.00	214.61	6.97	18.62
30.65	3.75	3.60	222.16	8.33	19.11
34.08	3.10	4.25	228.23	8.05	19.40
37.33	3.34	4.74	235.88	7.65	20.01
40.74	3.33	5.27		Series 2	
44.43	3.98	5.80	230.64	7.98	19.62
48.69	4.54	6.39	239.05	8.78	20.17
53.44	5.02	6.98	247.63	8.35	20.72
58.64	5.42	7.57	255.71	7.85	21.72
63.80	4.86	8.07	263.47	7.87	23.68
68.49	4.45	8.58	268.99	8.02	22.88[a]
73.21	4.98	8.94	287.66	4.78	32.63
78.01	4.64	9.25	293.00	6.93	32.72
83.28	5.95	9.63	299.22	6.67	33.25
84.20	5.87	9.67	305.67	6.89	33.54
90.32	6.28	10.01		Series 3	
96.27	5.85	10.49	238.27	4.47	20.12
102.29	6.23	10.94	242.86	4.66	20.49
108.36	5.86	11.37	247.51	4.56	20.82
114.47	6.23	11.77	251.99	4.45	21.06
120.59	5.89	12.22		Series 4	
127.04	6.95	12.65	254.73	6.15	21.73
133.82	6.47	13.11	259.55	3.54	22.47
140.45	6.89	13.56	261.79	1.58	24.36
147.45	7.19	14.03	263.38	1.60	23.32
154.41	6.83	14.50	265.04	1.63	22.56
161.05	6.46	15.03	269.59	5.47	23.03
167.65	6.83	15.53	275.23	5.12	24.68
174.56	7.11	15.85	279.78	3.91	34.08

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

Heat Capacity.—The heat capacity measurements were made in the usual manner. A small amount of helium 2–7 cm. pressure at ordinary temperatures, was added to the calorimeter to facilitate thermal conduction.

Results taken from a smooth curve through the observations are believed to be accurate to 3% near 15°K., 1% near 20, 0.1 to 0.2% above 35°K. The observations are given in Tables II, III and IV. The 1.6 mole % of tri- in the dihydrate required a small correction. Heat capacity results of Kunzler and Giauque[5] were available and the correction in the solid state was a simple matter of allowing for the presence of some crystalline trihydrate. Above the melting point of the dihydrate it was necessary to recognize the effect of solution imperfection on the mixture. This correction was also based on measurements of Kunzler and Giauque[7] as a function of concentration. The corrections did not exceed 0.2% but were of opposite sign in solid and liquid. The values in Tables II, III and IV do not include these corrections. The smoothed corrected values will be published later[8] as part of a thermodynamic treatment of the H_2SO_4–H_2O system. The smooth curves were drawn

TABLE III

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

T, °K	ΔT	C_p	T, °K	ΔT	C_p
	Series 1		159.82	5.81	18.51
14.87	1.29	0.57	165.71	6.03	19.12
16.62	2.09	0.75	171.95	6.47	19.66
18.65	1.95	1.04	178.50	6.67	20.20
20.81	2.40	1.41	185.01	6.36	20.83
23.43	2.93	1.85	191.50	6.56	21.44
26.11	2.41	2.29	198.26	6.97	22.06
28.94	3.18	2.81	205.14	6.66	22.68
32.30	3.43	3.47	211.73	6.39	23.21
35.93	3.73	4.20	218.03	6.18	23.68[a]
39.83	4.01	4.91	224.86	7.13	24.52[a]
43.98	4.28	5.61	231.74	6.50	26.58
48.50	4.83	6.37	238.36	6.53	25.67
53.45	5.12	7.20	244.89	6.28	26.27
58.49	4.99	8.00	251.34	6.55	27.02
63.46	4.90	8.73	257.97	6.79	27.60
68.38	4.89	9.39	264.74	6.95	28.49
73.57	5.50	10.04	271.55	6.90	30.21
78.83	5.03	10.66		Series 2	
84.22	5.76	11.26	218.11	6.55	23.84
89.84	5.62	11.82	224.89	7.03	24.51
95.61	5.89	12.44	229.25	3.42	24.86
101.66	6.16	13.10	233.08	3.36	25.19
107.95	6.41	13.75	236.39	3.29	25.49
114.47	6.63	14.42		Series 3	
121.19	6.85	15.07	268.24	8.02	29.45
128.13	7.02	15.71	275.70	7.14	31.90
134.87	6.58	16.32		Series 4	
141.20	6.19	16.90	284.02	5.92	50.81
147.51	6.41	17.41	290.47	6.95	51.03
153.86	6.08	18.00	297.52	7.18	51.27
			304.60	6.94	51.68

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

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(6) J. E. Kunzler and W. F. Giauque, THIS JOURNAL, **74**, 797 (1952).

(7) J. E. Kunzler and W. F. Giauque, *ibid.*, **74**, 804 (1952).

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

TABLE IV

HEAT CAPACITY OF $H_2SO_4 \cdot 2H_2O$ IN CAL. DEG.$^{-1}$ MOLE^{-1}

T, °K	ΔT	C_p	T, °K	ΔT	C_p
	Series 1		135.49	6.78	20.04
14.34	1.00	0.92	142.07	6.37	20.75
16.00	1.82	1.20	148.68	6.68	21.48
17.92	1.77	1.67	155.54	6.99	22.27
19.99	2.24	2.19	162.77	7.28	22.97
22.58	2.83	2.78	169.86	6.90	23.75
25.26	2.40	3.36	177.60	7.78	24.61
28.39	3.85	4.04	185.16	7.38	25.50
32.04	3.46	4.88	192.88	7.56	26.39
35.73	3.92	5.66	200.24	7.20	27.19
39.31	3.35	6.39	207.21	7.46	27.85
42.88	3.81	7.06	214.49	7.12	28.72
46.89	4.15	7.93	220.81	5.44	29.61
51.51	4.86	8.67	226.49	5.21	30.52
56.61	5.20	9.57		Series 2	
62.08	5.13	10.50	238.71	4.47	59.45
67.26	5.11	11.32	243.48	5.02	59.82
72.16	4.67	12.07	248.95	5.78	59.84
77.28	5.52	12.77	255.16	6.52	60.19
82.54	5.05	13.51	262.63	7.34	60.60
87.94	5.62	14.22	269.65	7.17	60.97
93.36	5.21	14.94		Series 3	
98.79	5.59	15.62	273.53	4.89	60.94
104.51	5.85	16.39	279.01	6.12	61.23
110.22	5.49	17.10	285.20	6.50	61.47
115.85	5.74	17.79	291.83	6.80	61.95
122.19	6.89	18.54	298.75	7.60	62.40
128.84	6.46	19.31	306.14	7.80	63.10

through values at 298.16°K. which were obtained from measurements of Kunzler and Giauque[7] at that temperature. This was done because these measurements are somewhat more accurate and because they tie in with data as a function of concentration. The agreement is very satisfactory. The measurements agree within the limit of error with the results of Biron[9] at 20°.

Heats of Fusion.—The heats of fusion were all measured in the usual manner of starting somewhat below the melting points and ending somewhat above. The fact that the compounds were slightly off the exact composition with respect to water content caused little difficulty but made it desirable to start well below the melting points to avoid large premelting corrections. The remaining small premelting corrections could be made from the heat capacity observations below the melting point. Other appropriate corrections were made for the presence of the small amounts of other hydrates but these produced no appreciable change in the results except in the case of the dihydrate where the presence of 1.6 mole per cent. of the trihydrate necessitated a correction of −13 cal. mole^{-1}.

There was no premelting in the heat capacity measurements below the melting point of the dihydrate, 233.69° K., since the highest observation stopped at 229.1°K. which is below the di–trihydrate eutectic temperature. This temperature has been given above as 230.40°K. which is in excellent agreement with the value 230.46°K. determined by Gable, Betz and Maron.[4] As mentioned above the existence of the trihydrate was unknown at the time the present measurements were made. Had the above eutectic been recognized it would have been used to check the amount of excess water in terms of eutectic melting. The di–monohydrate eutectic is even closer to the melting point. Gable, Betz and Maron[4] give its temperature as 233.29°K. which is only 0.4° below the melting point of the dihydrate.

In the case of two measurements of the heat of fusion of the dihydrate, which are not included here, the result was small by amounts of 176 and 202 cal. mole^{-1}, respectively. The substance had been cooled rapidly and had not been cooled to a very low temperature in these cases. The trihydrate present had evidently failed to crystallize. The supercooled solution of di- and trihydrate must have had approximately the eutectic composition since the discrepancy corresponds to about the heat of fusion of the amount of eutectic

TABLE V

HEATS OF FUSION OF SULFURIC ACID AND ITS MONO- AND DIHYDRATES

Initial temp., °K.	ΔH, cal. mole^{-1}
H_2SO_4, m.p. 283.53°K.	
275.33	2560
273.71	2561
273.95	2560
Accepted value 2560 ± 3	
$H_2SO_4 \cdot H_2O$, m.p. 281.64°K.	
275.59	4642
279.01	4645
277.53	4650
Accepted value 4646 ± 5	
$H_2SO_4 \cdot 2H_2O$, m.p. 233.69°K.	
225.04	4361
225.82	4359
Accepted value 4360 ± 4	

TABLE VI

THE ENTROPY IN CAL. DEG.$^{-1}$ MOLE^{-1} OF SULFURIC ACID AND ITS MONO- AND DIHYDRATES

H_2SO_4	
0–15°K., extrapolation	0.27
15–283.53°K., graphical	26.54
Fusion, 2560/283.53	9.03
283.53–298.16°K., graphical	1.65
	37.49
$H_2SO_4 \cdot H_2O$	
0–15°K., extrapolation	0.19
15–281.64°K., graphical	30.89
Fusion, 4646/281.64	16.50
281.64–298.16°K., graphical	2.91
	50.49
$H_2SO_4 \cdot 2H_2O$	
0–15°K., extrapolation	0.36
15–233.70°K., graphical	32.26
Fusion, 4360/233.70	18.66
233.70–298.16°K., graphical	14.76
	66.04

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(9) E. Biron, *J. Russ. Phys. Chem. Soc.*, **31**, 171 (1899).

which should have crystallized. The composition of the glass formed was of course a matter of chance. This occurrence illustrates how the tendency of the H_2SO_4–H_2O system to supercool complicates its study at low temperatures.

The values of the several heats of fusion are given in Table V.

The Entropy Calculations.—The entropy calculations are summarized in Table VI. The small amounts of entropy obtained by extrapolation below 15°K. were estimated by plotting C_p/T^3 against temperature since such a curve should approach the absolute zero without a slope.

It was found to be impossible to correlate the above entropy values by means of existing data which could be used for the free energy and heat changes of such reactions as

$$H_2SO_4 \cdot 2H_2O = H_2SO_4 \cdot H_2O + H_2O$$

It became evident that the solution of the above problem would require not only a new approach but repetition of much of the existing calorimetry on the sulfuric acid–water system at ordinary temperatures. The simplest method of obtaining the entropy change, ΔS, of a hydration reaction such as that given above is by means of the equation

$$\Delta S = \frac{\Delta H - \Delta F}{T}$$

where ΔH and ΔF are the heat and free energy of the reaction. Neither of these quantities were known with the accuracy required for the present work.

Kunzler and Giauque[7] have carried out a detailed investigation on the partial molal heat contents and heat capacities of sulfuric acid solutions.

These results and freezing point data have been combined to show that sulfuric acid and its mono- and dihydrates approach zero entropy at low temperatures. These calculations will be published later. In the meantime the entropy values given above may be accepted as the absolute entropies, less the nuclear spin and isotope effects as is customary.

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The Change in Electrical Conductivity of Aqueous Sulfuric Acid near Absolute H_2SO_4 and $H_2SO_4 \cdot H_2O$[1]

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The change in electrical conductivity of aqueous sulfuric acid has been compared experimentally with the freezing point lowering near the melting points and compositions of the compounds, H_2SO_4 and $H_2SO_4 \cdot H_2O$, utilizing a conductivity cell designed for use within a freezing point apparatus. Contrary to the conclusions of earlier workers, it has been shown that the minimum of electrical conductivity of concentrated sulfuric acid does not occur exactly at the composition of absolute sulfuric acid. The much larger difference in composition of the minimum of conductivity near sulfuric acid monohydrate and the monohydrate was also measured.

The composition relationship between absolute sulfuric acid and the minimum conducting solution near absolute acid has been of interest for some time. Hantzsch[2] found that the maximum of freezing point and minimum of conductivity were at the same composition, within the limits of his experimental accuracy. A little later Lichty[3] proposed the measurement of electrical conductivity as a means of analyzing aqueous sulfuric acid solutions near absolute sulfuric acid, and he took great pains to fix the position of absolute sulfuric acid in his conductivity table. Lichty found experimentally that stoichiometric quantities of carefully purified water and sulfur trioxide produced a solution of minimum electrical conductivity. We have found a small difference which is within Lichty's limit of accuracy.

The investigation of the freezing point composition diagram for the system H_2SO_4–H_2O[4] and the determination of other thermodynamic properties of aqueous sulfuric acid[5] require very accurate knowledge of the composition near absolute sulfuric acid. There is no basic reason why the minimum of conductivity should occur exactly at the absolute acid. Because of the interest in the problem and the facilities available, it was decided to investigate the amount of the deviation by direct comparison with the freezing point lowering.

Experimental

Preparation of Material Used.—Reagent grade sulfuric acid and 30% fuming sulfuric acid were purified by distillation in an all Pyrex system. Only the middle fractions were used. The purified acid was believed to have contained approximately 0.002 wt. % air when saturated and 0.0003 mole % solid-insoluble liquid-soluble impurity other than air. Details of the method of purification and determination of purity are given by Kunzler[6] in connection with absolute sulfuric as a primary analytical standard.

Apparatus.—A conductivity cell was designed for use within the freezing point apparatus employed by Kunzler and Giauque,[4] making it possible to measure the electrical conductivity of a solution of the same composition as that in equilibrium with solid H_2SO_4. This direct comparison feature eliminates uncertainties due to intermediate analytical procedures which otherwise would have been required.

The cell was made of Pyrex, with platinum electrodes sealed through cobalt glass. Each electrode was $^3/_4$ mm. diam. platinum wire in the form of a helix and had approximately three-tenths of a square cm. surface. The electrode surfaces were conditioned by electro-deposition

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[2] A. Hantzsch, *Z. physik. Chem.*, **61**, 257 (1907).

[3] D. M. Lichty, THIS JOURNAL, **30**, 1845 (1908).

[4] J. E. Kunzler and W. F. Giauque, data to be published.

[5] W. F. Giauque, J. E. Kunzler and T. R. Rubin, data to be published.

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