

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

Aqueous Sulfuric Acid. Heat Capacity. Partial Specific Heat Content of Water at 25 and  $-20^{\circ}$ <sup>1</sup>

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The heat capacity of aqueous sulfuric acid and the partial specific heat content of water has been determined over the range 1 molal to pure  $H_2SO_4$  at  $25^{\circ}$ . Some concentrations, still liquid at  $-20^{\circ}$ , were investigated at that temperature. The measurements were made to enable the calculation of the change in the partial molal free energies of the components from freezing point data of the various hydrates. An improved calorimeter and procedure for making such measurements is described.

The investigation reported here had its origin in unsuccessful attempts to use existing data to evaluate the entropy of hydration of sulfuric acid. The entropy of hydration was desired for comparison with results obtained from low temperature heat capacities and the third law of thermodynamics. The most promising method of obtaining the entropy of hydration, especially in the more concentrated solutions, depends on the use of freezing point data on the several hydrates. The freezing point curves have been investigated by Gable, Betz and Maron.<sup>2</sup> However, these authors did not plan their measurements for the purpose of obtaining partial molal free energies and their observations are being supplemented by additional measurements, especially in the important regions near the melting points of the monohydrate and the anhydrous acid.

The free energy and entropy calculations will be presented in a later paper. The calculations require an accurate knowledge of the partial molal heat contents and heat capacities in sulfuric acid solutions. Data are available, but on trying to use the basic observations we found that it was impossible to reproduce the partial molal quantities given in the tables of Lewis and Randall,<sup>3</sup> and by Craig and Vinal<sup>4</sup> in an unambiguous manner.

A principal difficulty is that total heat values given by Brönsted,<sup>5</sup> and others, and total heat capacities given by Biron,<sup>6</sup> were not measured at sufficiently close intervals. Many additional values are required to permit the accurate derivation of the partial molal quantities by differentiation of the total quantities with respect to concentration. The available calculations also contained detectable arithmetical errors.<sup>7,8</sup>

It became evident that in order to obtain the

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

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

(3) G. N. Lewis and M. Randall "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, N. Y., 1923, Chap. VIII.

(4) D. N. Craig and G. W. Vinal, *J. Research Natl. Bur. Standards*, **24**, 475 (1940).

(5) J. N. Brönsted, *Z. physik. Chem.*, **68**, 693 (1910).

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

(7) It may be shown that Brönsted<sup>5</sup> gave  $n$  (moles  $H_2O$  per mole  $H_2SO_4$ ) as 1.993 (Table V) when it should have been 2.016. This leads to a value of 9970 instead of 10020 cal. mole<sup>-1</sup> for  $n = 2$  in his Table VII.

(8) F. R. Bichowsky and F. D. Rossini, "The Thermochemistry of Chemical Substances," Reinhold Publishing Corp., New York, N. Y., 1936. Bichowsky and Rossini made an additional error equivalent to 1 kg. in quoting Brönsted's value for  $n = 2$  and this value was used by Craig and Vinal<sup>4</sup> in their calculations and affects their results from  $n = 2$  to  $n = 9$ .

accuracy needed in the present research, the partial molal properties would have to be redetermined. The method adopted was making small increments of water to the sulfuric acid solution, observation of the temperature rise, subsequent cooling, followed by the introduction of electrical energy to evaluate the heat of solution and the heat capacity. It was clear that diluting sulfuric acid by small increments, over the whole range of concentration, would require some improvement over previous procedure in order to bring the amount of experimental work within reasonable limits. Such a method as bringing a sample of water to temperature equilibrium within the calorimeter, with subsequent mixing, is impracticable, not only because of the labor involved, but also because the repeated disassembling and assembling of the necessarily somewhat fragile apparatus would cause its deterioration.

**The Dilution Calorimeter.**—The calorimeter was designed along the lines of one used by Randall and Bisson<sup>9</sup> for dilution experiments. The details of the present calorimeter are indicated in Fig. 1. The dilution is carried out in a one liter silvered dewar, 7, which was specially constructed without spacers, to reduce heat leak. The dewar is enclosed in a nickel plated brass container, 4. The shaft of a Pyrex glass stirrer, 9, was sealed to a brass shaft, 3, by de Khotinsky cement at a point under a clamp which supports a rubber cup, 5. This cup is used to catch any grease or dirt that might work its way down the stirrer shaft. Reliable stirrer operation and uniform speed are essential in such an apparatus, and these were not obtained until an "Oilite" bearing just below position 3 of Fig. 1, was installed.

Before obtaining the electrical equivalent of the temperature rise, accompanying a reaction, the calorimeter must be cooled. We found no previous procedure for cooling which was not open to objection as a general method.

The method of cooling the calorimeter by cooling the surroundings (*i.e.*, the thermostat) is extravagantly slow if the calorimeter is properly insulated. Moreover in dilute solutions where the vapor pressure approaches that of the solvent, distillation may occur to the top of the calorimeter. Still worse, this may lead to unmeasurable heat effects during the following experiment as the material distills back to the solution, which will be colder than the top during at least a portion of the measurement.

The above difficulty can be largely avoided by cooling through the vacuum evaporation of water in a bulb immersed in the calorimeter. However this method, which was used by Barieau and Giauque,<sup>10</sup> is also too slow if a large number of observations is to be made.

Randall and Rossini<sup>11</sup> and Randall and Taylor<sup>12</sup> cooled calorimeters of this general type with a stream of cold air (cooled by liquid air) which passed through a coil immersed in the solution within the calorimeter. This is a desirably rapid method but preliminary experiments showed that

(9) M. Randall and C. S. Bisson, *THIS JOURNAL*, **42**, 347 (1920).

(10) R. E. Barieau and W. F. Giauque, *ibid.*, **72**, 5676 (1950).

(11) M. Randall and F. D. Rossini, *ibid.*, **51**, 323 (1929).

(12) M. Randall and M. D. Taylor, *J. Phys. Chem.*, **45**, 959 (1941).

water distilled to the upper portion of the tube carrying the cold air. This was found to cause the same objectionable delayed reverse distillation effects mentioned above. It seems likely that Randall and his co-workers<sup>11,12</sup> allowed a long time for equilibrium after cooling the calorimeter since their data appear to be quite accurate. However, waiting a long time largely nullifies the advantage of the method as they used it.

In the present apparatus the difficulty was avoided by passing a stream of nitrogen gas, cooled by liquid nitrogen, down the inner of two concentric tubes shown at 6, in Fig. 1. The outer tube, which carried the exit gas in the annular space between the tubes, was kept warm by means of an electrical heater. The inner tube had a diameter of 1 mm. and a very thin wall. It happened to be made of nickel which was available. The outer tube was of glass, 3 mm. i.d. The heater consisted of a closely wound coil of no. 36 insulated Manganin wire, which was sprung into place inside the glass tube. In order to obtain rapid cooling the nitrogen inlet had a pressure of 1.4 atmospheres and the exit tube was attached to a vacuum. These conditions were stable and it was found that a current of 0.30 ampere through the coil would prevent water from condensing on the tube when the air was saturated. The heating coil extended from just above the maximum solution level to a height of about 2.5 cm. above the top of the dewar. It had a resistance of 280 ohms.

In the concentrated and fuming regions water was introduced by means of a capillary tube 0.5 mm. i.d. The arrangement was such that the water should have entered the solution at thermostat temperature. The water reservoir, II, Fig. 1, was attached to the capillary at the ground glass female joint, 1. The water in the weight reservoir was within two- or three-tenths of a degree of thermostat temperature before it entered the thermostated capillary tube. Assuming that it failed to reach thermostat temperature by  $0.1^{\circ}$ , the resulting error would be about two parts in ten thousand in the range where it was used. In the moderately concentrated range, where larger samples of water were added, a small pressure of nitrogen increased the rate of introduction. The tubes were cleared of water by the use of small and definitely measured amounts of nitrogen gas under a small measured pressure. Increments totaling 10 to 12 cm.<sup>3</sup> of nitrogen sufficed to clear the tubes. Preliminary investigation showed that not over 1 mg. of water remained in the capillary and that a small droplet of about 2 mg. sometimes remained in the female joint. Even such small amounts were not lost but entered the calorimeter during the following measurement since the joint was kept covered between experiments.

In the more dilute range, where larger increments of water were used, it was necessary to replace the capillary tube referred to as 1 of Fig. 1 by a vacuum jacketed transfer tube, 2, in order to introduce the water within a reasonable time. Had the diameter of the capillary been increased, it would have been difficult for the water to attain thermostat temperature. With the vacuum jacketed tube, which was silvered, the water entered the calorimeter essentially at the temperature of the weight reservoir. The weight reservoir used with the vacuum jacketed tube had a built in thermometer which could be interpolated to thousandths of degrees. It was similar to the one shown in II of Fig. 1.

The Pyrex glass transfer tube, 2, Fig. 1, had an inner tube 0.13 cm. i.d. with a 0.06 cm. wall. The outer tube was 0.53 cm. o.d. with a 0.09 cm. wall. The heat capacity of the inner tube was negligible in comparison with that of the approximately 100-g. samples of water used for measurements near  $25^{\circ}$  in the dilute region. Blank experiments in which water samples were introduced into water showed that the temperature of the water entering the calorimeter through the transfer tube was known to within  $0.01^{\circ}$ . Before introduction, the water in the weight reservoir was stirred occasionally by means of a platinum wire stirrer kept in the reservoir to ensure uniform temperature.

The problem of knowing the temperature in the weighing reservoir was greatly simplified by having the room thermostat at the same temperature ( $25^{\circ}$ ) at the water thermostat. This required the use of a balancing cold water coil in the water thermostat.

The temperature difference between the thermostat and the calorimeter was observed by means of a copper-constantan thermocouple. The temperature of the calorimeter was measured by means of an annealed copper resistance

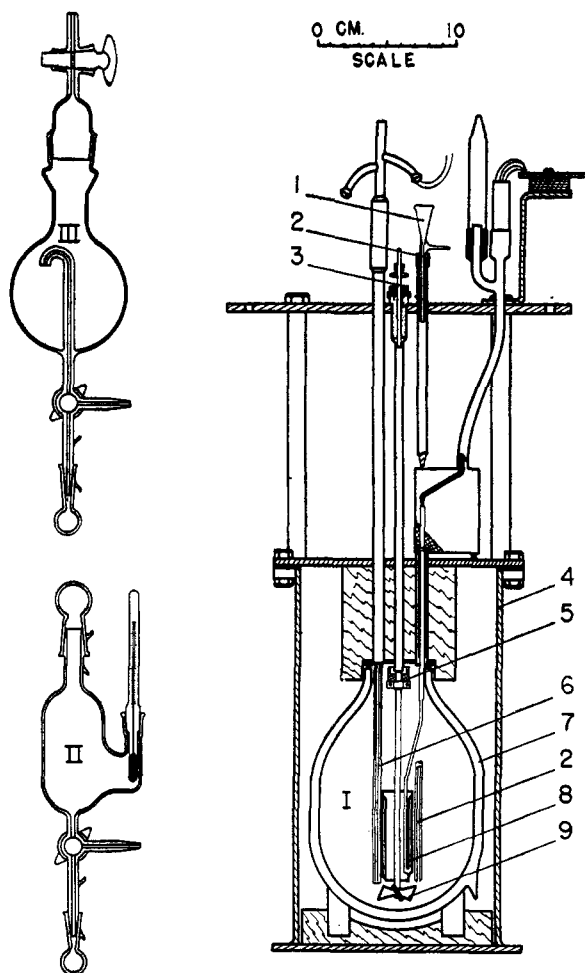


Fig. 1.—Differential dilution calorimeter: I, calorimeter; II, weighing reservoir for adding water; III, weighing reservoir for removing solutions.

thermometer-heater, 8, Fig. 1, enclosed in a platinum case. This resistance thermometer-heater has been described previously.<sup>13</sup> The fixed points given in Table I were used in calibrating the thermometer so that heat capacity measurements could be given absolute values.

TABLE I

Temperature, °K.	Substance and condition
194.65	CO <sub>2</sub> , sublimation at 1 atm.
234.29	Hg, melting point
273.16	Ice point
305.54	Na <sub>2</sub> SO <sub>4</sub> ·10H <sub>2</sub> O, transition
395.52	Benzoic acid, melting point

After long standing in sulfuric acid, this thermometer broke down electrically and a trace of sulfuric acid was found inside. Fortunately no measurements were in progress near this time; however, two other somewhat similar failures of platinum tubing in concentrated sulfuric acid in this Laboratory justify some suspicion concerning a reaction between platinum and concentrated sulfuric acid. Particles of impurity dissolving out could possibly explain the effect but this seems improbable.

Some dilution measurements were made at  $-20^{\circ}$  and for this work the water in the thermostat was replaced by 50 volume % ethyl alcohol cooled by means of a Freon-12 refrigeration unit. During the measurements at  $-20^{\circ}$ , the water entered the calorimeter through the vacuum jacketed

(13) W. F. Giauque and R. C. Archibald, *THIS JOURNAL*, **59**, 561 (1937).

transfer tube at 25°. In this case the heat capacity of the inner tube of the transfer tube could not be entirely neglected. At the start of an experiment the inner tube was 25° at one end and -20° at the other. Immediately after the water at 25° passed through it the glass was left at that temperature. In order to avoid possible freezing of traces of water, not ejected by the nitrogen gas, the acid solution in the calorimeter at -20° was sucked up just to the top of the tube. When this solution was blown back to the calorimeter by a very small amount of nitrogen, the final minus initial heat content of the tube could be estimated. The correction to the partial molal heat content values due to this effect was approximately 0.1%. This could be minimized by reducing the amount of glass in the inner tube.

**The Heat Capacity of the Calorimeter.**—In many types of calorimeters the heat capacity is a definite quantity which is a function only of temperature. When a dewar is used as a calorimeter, as is customary in heat of dilution and heat of reaction measurements, the heat capacity of the vessel is also a function of the amount of liquid which the calorimeter contains. There is no definite boundary between the inside and the outside of the calorimeter. The portions of the dewar wall above the liquid, the neck and the various tubes, shaft, etc., represent an appreciable amount of heat capacity in the intermediate temperature region. The effective heat capacity may be determined as a function of liquid height by making measurements with various amounts of water or other liquids of known heat capacity in the dewar. The magnitude of this effect is shown in Table II.

TABLE II

HEAT CAPACITY OF CALORIMETER AS FUNCTION OF VOLUME FILLED AT 25°

Volume, cc.	C <sub>p</sub> , cal. deg. <sup>-1</sup>	Volume, cc.	C <sub>p</sub> , cal. deg. <sup>-1</sup>
650	32.30	850	33.12
700	32.45	900	33.75
750	32.60	950	35.00
800	32.80	1000	38.10

The heat capacity of water at 25° was taken as 0.9989 cal. deg.<sup>-1</sup> g.<sup>-1</sup> from the work of Osborne, Stimson and Ginnings.<sup>14</sup> Small corrections were made for the vaporization of water during the measurements with water and dilute sulfuric acid solutions.

At -20° the effective heat capacity of the calorimeter was obtained by using liquid H<sub>2</sub>SO<sub>4</sub>·3H<sub>2</sub>O, the heat capacity of which was known from other work.<sup>15</sup> The value was found to be 25.1 cal. deg.<sup>-1</sup> at -20° when the calorimeter contained 850 cc. The effective heat capacity of the calorimeter was not investigated as a function of volume filled at -20° and it was assumed that the variation at 25° would apply. When the detailed calculations were completed, it was found that the heat capacity at -20° was smaller than would be expected from the temperature coefficients of the materials concerned. We believe that at the higher temperature radiation increased the domain of the calorimeter to include portions of the neck, connecting tubes and cover which were not very effective at the lower temperature. This should have some effect on the variation of the heat capacity of the calorimeter as a function of volume filled. While the effect is a matter of interest as a point to be considered in calorimetry, it could not have had an appreciable effect on the present results due to the high ratio of substance to calorimeter. It was possible to confirm this by considering results obtained with compositions corresponding to H<sub>2</sub>SO<sub>4</sub>·2H<sub>2</sub>O and H<sub>2</sub>SO<sub>4</sub>·4H<sub>2</sub>O and a filling of about 700 cc. in each case. These substances were also measured in other calorimetric equipment in this Laboratory. The total filling range used at -20° was from 875 to 897 cc.

**The Partial Specific Heat Content of Water in Aqueous Sulfuric Acid.**—The average partial specific heat content of water in sulfuric acid was measured over rather small increments so that the differential values could be derived accurately.

(14) N. S. Osborne, H. F. Stimson and D. C. Ginnings, *J. Research Natl. Bur. Standards*, **23**, 245 (1939).

(15) J. E. Kunzler and W. F. Giauque, *This Journal*, **74**, 797 (1952).

All results were corrected to 25 or -20°. The heat content of water was taken as zero at 25° for measurements at both 25 and -20°.

One calorie was taken equal to 4.1833 international joules. The molecular weight of water was taken as 18.0160 and that of sulfuric acid as 98.082.

$$A = \frac{\text{moles H}_2\text{O} - \text{moles SO}_3}{\text{moles SO}_3} \text{ from } A = -1 \text{ to } A = \infty$$

$$= \text{moles H}_2\text{O}/\text{mole H}_2\text{SO}_4 \text{ from } A = 0 \text{ to } A = \infty$$

In accordance with the usual custom with sulfuric acid the weight % is taken as referring to the total weight of sulfuric acid which can be made from the total SO<sub>3</sub> present.

$$\text{Wt. \% H}_2\text{SO}_4 = \frac{\text{wt. SO}_3 \times 100}{\text{wt. SO}_3 + \text{wt. H}_2\text{O}} \times \frac{98.082}{80.066}$$

These definitions lead to negative values of *A* and more than 100% acid when the SO<sub>3</sub>/H<sub>2</sub>O ratio exceeds unity.

The data are given in Table III.

TABLE III

PARTIAL SPECIFIC HEAT CONTENT OF WATER IN AQUEOUS SULFURIC ACID

Water at 25° is taken as having zero relative heat content

A	Av. comp. av., cal. g. <sup>-1</sup>		- $\bar{L}_1$ av., cal. g. <sup>-1</sup>	
	$\frac{\text{moles H}_2\text{O}}{\text{mole H}_2\text{SO}_4}$	$\Delta A$	$\frac{\text{moles H}_2\text{O}}{\text{mole H}_2\text{SO}_4}$	$\Delta A$
Series 1 at 25°				
0.2023	0.04388	413.9	-0.01025	0.00263 967
.2465	.04448	409.0	-.00796	.00193 959
.2902	.04308	402.8	-.00585	.00230 954
.3331	.04263	396.7	-.00372	.00197 926
.3751	.04262	391.2	-.00166	.00215 866
.4194	.04478	384.3	.00065	.00246 685
.4637	.04388	378.2	.00302	.00227 533
.5068	.04221	371.4	.02316	.03802 446.6
.5504	.04510	363.9	.05780	.03125 435.1
.5951	.04421	356.0	.09164	.03643 430.5
.6384	.04231	347.5	.12776	.03581 425.8
.6798	.04049	340.5	.1632	.03499 420.6
.7224	.04488	331.6	.1999	.03749 415.5
.7668	.04373	321.0	.2322	.03665 411.2
.8117	.04614	310.5	Series 4 at 25°	
.8594	.04922	298.0	2.6121	0.3540 93.06
.9077	.04738	287.3	3.0151	.4520 78.66
.9547	.04663	273.9	3.5368	.5913 64.69
.9999	.04375	264.6	4.3712	1.0775 49.66
1.0454	.04737	253.5	5.5870	1.3541 35.89
1.0924	.04666	242.0	7.9086	3.2891 21.07
1.1394	.04717	232.0	11.989	4.8712 9.07
1.1897	.05353	221.4	17.907	6.965 3.35
1.2476	.06223	210.3	26.111	9.440 1.24
1.3119	.06638	199.31	Series 5 at 25°	
1.3822	.07319	187.77	15.143	5.204 5.00
1.4654	.09424	175.97	21.869	8.247 1.98
1.5555	.08609	164.78	31.348	10.812 0.78
1.6499	.10264	154.49	45.083	16.558 .36
1.7539	.10541	144.31	64.892	23.06 .20
1.8680	.12261	134.77	93.015	33.19 .11
1.9974	.13639	125.21	133.41	47.60 .06
2.1421	.15284	115.70	Series 6 at -20°	
2.3094	.18185	106.67	1.9599	0.3223 160.8
2.4989	.19709	97.01	2.2462	.2504 144.6
Series 2 at 25°				
-0.13336	0.01591	952.3	2.5965	.4502 129.8
-.11645	.01791	953.3	3.0436	.4440 115.3
-.09998	.01503	954.0	3.5926	.6540 102.9
-.08309	.01875	954.3	4.2628	.6864 92.1
-.06481	.01781	954.0	5.1317	1.0513 83.0
-.04742	.01696	954.7	6.3908	1.4669 74.0
-.03036	.01717	956.1	8.1314	2.0143 65.8
			10.725	3.1721 56.4

As a check on the values of  $\bar{L}_1$  at  $-20^{\circ}$ , calculations were made on the basis of values of  $\bar{L}_1$  at  $25^{\circ}$  and a linear variation of  $\bar{C}_p$  between  $25$  and  $-20^{\circ}$ . The differential values of  $\bar{L}$  and  $\bar{C}_p$  at  $25$  and  $-20^{\circ}$  will be published later. A comparison of observed and calculated values of  $\bar{L}_1$  av. at  $-20^{\circ}$  is given in Table IV. The values of  $\Delta A$  in Table IV are the same as those given in Table III. The calculated values at the upper and lower ends of Table IV are somewhat less reliable than the others because of difficulty in obtaining the derivative of  $C_p$  at the ends of the curve at  $-20^{\circ}$   $\bar{C}_p = (\partial C_p / \partial m_1)_{m_2}$ .

TABLE IV

OBSERVED AND CALCULATED VALUES OF PARTIAL MOLAL HEAT CONTENT OF WATER IN AQUEOUS SULFURIC ACID AT  $-20^{\circ}$  IN CALORIES MOLE $^{-1}$

A av.	$\bar{L}_1$ av. obsd.	$\bar{L}_1$ av. calcd.
1.9599	2900	2885
2.2462	2608	2597
2.5965	2341	2340
3.0436	2078	2087
3.5926	1856	1860
4.2628	1661	1667
5.1317	1496	1498
6.3908	1334	1338
8.1314	1187	1188
10.725	1016	1026

**The Partial Heat Content of Water in and near Absolute Sulfuric Acid.**—On the basis of previous work practically nothing is known concerning the partial heat content of water in the region near absolute sulfuric acid. As part of the present work a narrow range on each side of the absolute acid was investigated to obtain the shape of the  $\bar{L}_1$  curve as a function of composition. The value of  $\bar{L}_1$  changes by about 8000 cal. mole $^{-1}$  when some 0.007 mole of water is added per mole of  $H_2SO_4$ . A special series utilized increments of about 0.002 mole of water per mole of  $H_2SO_4$  (15 moles in calorimeter) in order to define the shape of the curve.

The location of the curve with respect to the composition corresponding to absolute sulfuric acid was a matter of considerable difficulty. The over-all curve was measured with C.P. acid. Later the position only was checked with respect to composition with distilled absolute acid standardized in terms of the freezing point maximum. A comparison of the above and other reference analytical standards has been discussed elsewhere.<sup>16</sup> Comparison of the above experiments led to the conclusion that the curve obtained with the C.P. acid was displaced by 0.019 wt. %. Since all analyses were finally referred to the same standard it was concluded that the C.P. acid contained 0.019 wt. % impurity. There is no reason to believe that this would appreciably alter the shape of the curve. It is believed that the curve is located with respect to the absolute acid within 0.005 wt. %.

A source of error in the above series was due to difficulty in accomplishing the complete introduction of such small quantities of water as 0.03 mole. Greater accuracy could be obtained by diluting with concentrated acid rather than water so that the

actual amount of material added would not be an appreciable source of error. This method was utilized in an auxiliary apparatus used to locate the curve by relative measurements. It became impracticable to repeat the whole curve by this method due to the electrical breakdown in the resistance thermometer of the principal calorimeter, which has been referred to above. The principal impurity in the distilled acid was believed to be dissolved air. This was determined in connection with the analytical procedure<sup>16</sup> to be 0.002 wt. %.

The measurements near absolute acid are given above in Table III as the first seven of series 3. A curve describing the detailed shape of  $\bar{L}_1$  near absolute sulfuric acid is shown in Fig. 2. The eighth measurement of series 3, which is not shown in Fig. 2, helped define the shape of the curve between  $A = 0.004$  and 0.042.

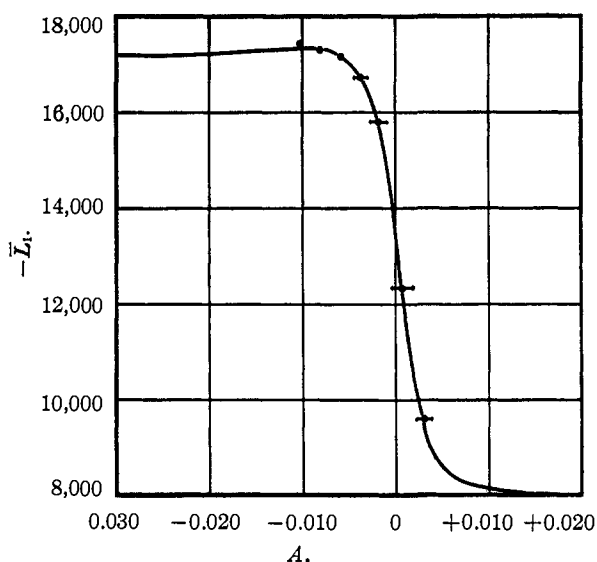


Fig. 2.—Partial molal heat content of  $H_2O$  in  $H_2SO_4$ ;  $\bar{L}_1$  in calories mole $^{-1}$ ;  $A$  = moles  $H_2O$  per mole  $H_2SO_4$ .

The short runs used to define the shape of the curve near absolute sulfuric acid may be in error by about 1%.

**The Heat Capacity of Aqueous Sulfuric Acid.**—The heat capacity of aqueous sulfuric acid was measured near  $25^{\circ}$  from 10 to 102.7% and near  $-20^{\circ}$  from 30 to 75%. The results, corrected to the even temperatures, are given in Table V.

Series 1, 2 and 3 were made before the tube heater, mentioned above, was installed in the nitrogen cooling system. With the concentrated solutions there was no water condensation on the exit tube. At the low acid concentrations in series 3a and 3b condensation did occur and from 5 to 10 hr. were used to clear the apparatus of this effect. Alterations between series 3a and 3b produced a small change in the water equivalent of the calorimeter. This was evaluated by measurements overlapping the previous range in series 3a. It became evident that the cooling nitrogen exit tube heater was a necessity and it was used in series 4 and 6. A re-determination of the water equivalent in terms of water was carried out after the tube heater was installed.

(16) J. E. Kunzler, *Anal. Chem.*, **24**, in press (1952).

**The Anomaly in the Heat Capacity near Absolute  $H_2SO_4$ .**—In Fig. 3 the specific heat of sulfuric acid over the range 98.5 to 101.5 wt. % is shown graphically. A small but sharp rise is indicated in the region near 100% acid. This effect was not large enough to attract attention during the experimental work or a more detailed study would have been made, especially in the region above 100%. The two overlapping series below 100% show excellent agreement.

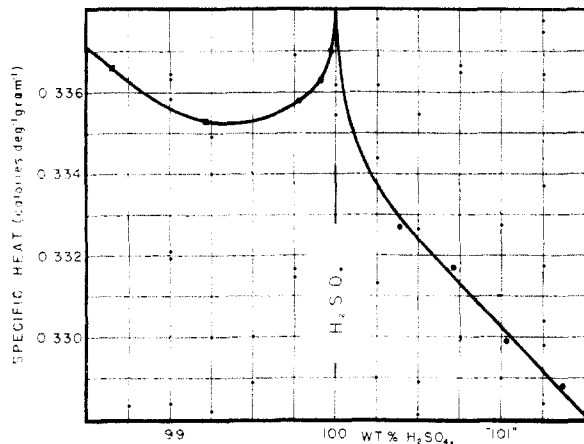


Fig. 3.—Specific heat of aqueous sulfuric acid near absolute  $H_2SO_4$ : ●, series 2; ■, series 3.

The rise in the curve at absolute  $H_2SO_4$  indicates that a small part of the heat capacity of absolute sulfuric acid is due to the temperature coefficient of the heat required for the dissociation of this substance. Either above or below 100% the dissociation is evidently repressed by increasing concentrations of the dissociation products characteristic of the two respective regions.

The type of effect observed here should become sharper and smaller as the dissociation constant decreases. For example, it would be too small for observation by ordinary methods in a substance with a dissociation as small as that of water. When the dissociation is very large the effect will be so broadened that its separation from other sources of heat capacity is likely to be difficult. The dissociation of sulfuric acid happens to fall in

TABLE V  
HEAT CAPACITY OF AQUEOUS SULFURIC ACID IN CAL.  
DEG.<sup>-1</sup> G.<sup>-1</sup>

$H_2SO_4$ wt. %	$C_p$ 25°	$H_2SO_4$ wt. %	$C_p$ 25°	$H_2SO_4$ wt. %	$C_p$ 25°
Series 1		Series 1 (Cont.)		Series 3a (Cont.)	
96.05	0.3499	76.19	0.4570	13.457	0.8895
95.30	.3549	75.08	.4602	13.457	.8905
94.59	.3594	73.84	.4627	10.775	.9101
93.89	.3647	72.49	.4674	10.775	.9126
93.20	.3703	71.05	.4723	Series 3b	
92.49	.3764	71.05	.4733	29.075	0.7742
91.81	.3823	71.05	.4721	22.545	.8228
91.16	.3881	69.40	.4787	17.350	.8616
90.48	.3946	Series 2		13.192	.8917
89.82	.3996	102.66	0.3247	10.127	.9142
89.20	.4068	102.35	.3255	Series 4	
88.61	.4133	102.05	.3270	66.12	0.4940
87.96	.4184	101.72	.3278	62.68	.5117
87.35	.4237	101.37	.3288	58.69	.5360
86.71	.4285	101.03	.3299	52.58	.5777
86.03	.4346	100.71	.3317	46.499	.6262
85.39	.4384	100.39	.3327	36.301	.7149
84.77	.4420	99.97	.3370	27.401	.7877
84.20	.4442	99.78	.3358	Series 6 $C_p - 20^\circ$	
84.20	.4430	Series 3		75.17	0.4400
83.59	.4464	99.91	0.3363	71.96	.4519
82.99	.4482	99.22	.3353	69.66	.4636
82.40	.4491	98.65	.3366	65.86	.4827
81.74	.4501	98.01	.3406	62.51	.5020
80.98	.4507	97.38	.3422	58.14	.5302
80.19	.4515	96.77	.3447	54.17	.5537
79.33	.4531	96.13	.3489	49.040	.5900
79.33	.4519	95.51	.3526	43.156	.6343
79.33	.4533	Series 3a		37.333	.6834
78.26	.4542	13.457	0.8909	30.662	.7346
77.30	.4558	13.457	.8878		

the intermediate region and the effect is sharpened enough to be noticeable.

Values of the partial molal heat capacity of sulfuric acid have been calculated from the results in Table V. These will be included in a later paper where they will be used in combination with other data to determine thermodynamic properties of aqueous sulfuric acid.

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