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.

We thank J. E. Kunzler, D. L. Hildenbrand and R. H. Busey for assistance with the calculations.

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

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

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

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

(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.

of platinum. Shielded leads from the cell to the bridge were protected from the solution by Pyrex glass tubes and made contact with the electrodes in small mercury pools.

The center section of the cell was constricted in area to decrease the total conductivity of the solution in the cell and to reduce current density at the electrodes. The total conductivity of such a cell could be decreased several fold by merely reducing the cross-sectional area of the center tube; however, wall effects would eventually become appreciable.

An opening at the bottom of the cell contained a medium-fine sintered glass filter through which the cell was filled with samples from the solid–liquid equilibrium mixture in the freezing point apparatus. This continuously stirred mixture also served as an excellent constant temperature environment.

A capillary tube leading from the top of the cell was used for applying dry air pressure or vacuum to empty or refill the cell. The air used for emptying the cell was extremely dry.

The measurements were made with 900 cycle a.c., using a Kohlrausch-type bridge and an oscilloscope as the null point detector.

Measurements.—A mixture of fine crystals (approx. 25% by wt.) in slightly SO_3-rich sulfuric acid was prepared from the purified material, repeating the method used for preparing freezing point mixtures.[4] The freezing point was observed, by means of a ten-junction copper–constantan thermocouple, both before and after each conductivity measurement. Although the solution was continuously stirred, the amount of solid melted was insignificant with respect to producing any change in composition or equilibrium temperature during any individual conductivity measurement.

TABLE I

FREEZING POINT LOWERING AND ELECTRICAL CONDUCTIVITY OF AQUEOUS SULFURIC ACID NEAR ABSOLUTE H_2SO_4

Total ml. concd. H_2SO_4 added	Observations F.p. lowering, °C.	Observations Resistance, ohms at f.p.	Composition, wt. % H_2SO_4	Resistance corrected to m.p., 10.37° C.
12.0	0.0217	1364.0	100.0179	1362.8
13.0	.0142	1376.7	100.0142	1375.9
14.0	.0082	1389.2	100.0106	1388.8
14.6	.0053	1395.1	100.0084	1394.8
15.25	.0029	1401.0	100.0061	1400.8
15.75	.0013	1407.1	100.0039	1407.1
16.0	.0006	1408.8	100.0027	1408.8
16.25	.0003	1411.1	100.0017	1411.1
16.50	.0001	1412.6	100.0006	1412.6
16.75	.0001	1414.2	99.9994	1414.2
17.0	.0002	1415.6	99.9984	1415.6
17.3	.0005	1416.5	99.9975	1416.5
17.75	.0013	1416.5	99.9959	1416.4
18.5	.0038	1415.8	99.9931	1415.6
19.5	.0090	1410.4	99.9895	1409.9
22.0	.0303	1381.9	99.9805	1380.3

The composition was changed by adding a measured volume of 96.20 wt. % sulfuric acid. Equilibrium was re-established in a matter of a minute or two. After allowing two additional minutes, the conductivity cell was filled, flushed and refilled. The filled cell was allowed to stand five minutes before accepting the conductivity measurement.

The observations for the composition near absolute sulfuric acid are given in the first 3 columns of Table I. The first column gives the total number of ml. of 96.20 wt. % sulfuric acid which was added. The second column contains the freezing point lowering and the third column expresses the conductivity in the form of the total resistance of the solution in the cell at the temperature of the freezing point.

The fourth column gives the composition of the solution corresponding to the freezing point lowering (column 3) determined by means of the freezing point–composition measurements of Kunzler and Giauque.[4] The conductivity measurements were placed on an isothermal basis by using the approximate temperature coefficient of −(3.9 ± 0.3) % per degree of some unpublished exploratory measurements. The data given in column 5 of Table I were corrected to the melting point, 10.37°.

The freezing point mixture near the composition of the monohydrate was prepared similarly to that near the absolute acid.[4] The measurements recorded in Table II were also similar except that the conductivity is tenfold greater and it changes very much less with composition. This necessitated nearly one hundred-fold greater changes in composition, which were made by adding water as noted in the first column. The derived values (last 2 columns of Table II) were obtained from the observations in essentially the same manner as described for data near the absolute acid (Table I), except that an observed value of −(4.03 ± 0.2) % per degree was used as the temperature coefficient of the resistance for correcting the observed resistance (column 3) to that at the melting point of the monohydrate (column 5). This value is the average of values obtained by changing the composition and therefore the temperature of the mixture in the freezing point apparatus without emptying the conductivity cell. Thus, the resistance of each sample of the solution was measured at two temperatures. Only the temperature coefficients calculated from the first two and last two samples were used for the average given above. The temperature differences were not large enough for the other samples.

TABLE II

FREEZING POINT LOWERING AND ELECTRICAL CONDUCTIVITY OF AQUEOUS SULFURIC ACID NEAR $H_2SO_4 \cdot H_2O$

Total ml. H_2O added	Observations F.p. lowering, °C.	Observations Resistance ohms at f.p.	Composition wt. % H_2SO_4	Resistance, corrected to m.p., 8.49°C.
5.0	0.384	122.77	85.39	120.88
9.0	.207	122.15	85.14	121.14
15.0	.053	121.59	84.82	121.33
18.0	.015	121.48	84.66	121.41
20.5	.001	121.39	84.52	121.39
23.0	.003	121.34	84.40	121.33
27.0	.032	121.35	84.21	121.19
32.0	.111	121.48	83.97	120.94
40.0	.314	121.94	83.64	120.41

The measurement of temperature coefficient of conductivity on the water side of the monohydrate involved supercooling of the sample in the cell. Experience has shown that the monohydrate is very difficult to crystallize after

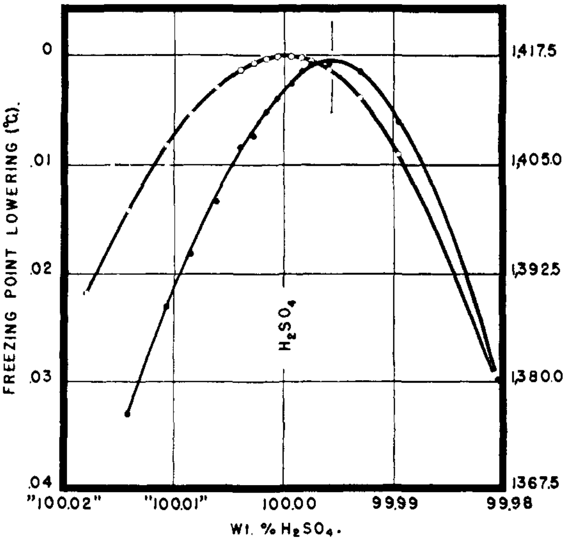

Fig. 1.—Resistance of solution in cell compared with freezing point lowering near absolute sulfuric acid: ○, freezing point lowering; ●, resistance.

complete melting. For this reason, and others involving the measurements themselves, it is quite certain that the cell remained free of crystals.

Results and Discussion

The experimental values of the total resistance of the solution in the cell corrected to the melting point, and the freezing point lowering near absolute sulfuric acid, are plotted against the composition in Fig. 1 (data in Table I.) The maximum in resistance (minimum in electrical conductivity) can be taken as occurring at 99.996 ± 0.001 wt. % sulfuric acid if it is assumed that the 0.002 wt. % air present is inert with respect to electrical conductivity. Any future investigation should be made under such conditions that the samples in both the freezing point apparatus and conductivity cell can be kept free of air.

No attempt was made to determine the cell constant, but the values of the resistance near the absolute acid (Fig. 1) are believed to be accurate, relative to each other, since the temperature coefficient corrections were very small. This is not true of the values near the monohydrate because the temperature correction was nearly as large as the differences themselves.

The minimum of electrical conductivity near the monohydrate was found to occur at 84.63 ± 0.05 wt. % H_2SO_4 (monohydrate is 84.48% H_2SO_4). It is of interest to note that the minimum near absolute acid is on the water side while the minimum near sulfuric acid monohydrate is on the sulfuric side.

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The Heat of Reaction of Graphite and Potassium

BY L. QUARTERMAN AND W. PRIMAK

The heat of reaction of graphite with an excess of potassium has been carefully redetermined, and it has been shown that the result given in the literature is considerably in error. The present determinations were made at several temperatures in the range 66–95°. For high density Acheson graphite, a mean value of 81 ± 2 cal./g. was obtained. There seemed to be a variation of about 5% in the heat of reaction of samples obtained from the same bar. The heat capacity of the calorimeter was found to have increased 0.25 ± 0.01 calorie for each gram of graphite introduced. Heats of reaction of some disordered forms of graphite were also determined and results some 15% lower than for Acheson graphite were indicated.

Introduction

Graphite–potassium compounds were studied by Fredenhagen and Cadenbach,[1] Fredenhagen and Suck[2] and Schleede and Wellman.[3] The heat of reaction of graphite with potassium was determined by Fredenhagen and Cadenbach.[1] They reported that 1500 cal. (± 5%) were released for each mole of carbon in the form of graphite introduced into an excess of potassium at a few degrees above its melting point. They also determined the heat of fusion of the potassium before and after introducing the graphite. From the ratio of this difference to the weight of graphite, they concluded the formula of the compound formed was close to KC_4. The present paper describes a redetermination of the heat of reaction of graphite and potassium.

Experimental

Apparatus.—Refinements were introduced into the apparatus during the course of the successive determinations. The calorimeter described is that used in the final determinations. The essential parts of the calorimeter are shown in Fig. 1.

The calorimeter consisted of a conical platinum cup A, about 20 cc. capacity, standing in an evacuated Pyrex tube B, 48 mm. o.d., with tubulations for evacuation C, for introduction of leads D and E, for introduction of potassium F, and for introduction of samples G.

The apparatus was connected to a large diffusion pump with a large cock intervening. A side arm led to a reservoir from which helium, stored over potassium, could be admitted to permit a rapid equalization of the calorimeter with the bath temperature.

Graphite samples were delivered from a side tube placed at the top of the apparatus. A sample size was chosen which would give approximately a 2° temperature rise on reaction. Graphite samples which could be machined were turned to suitable diameter (3–4 mm.) on a lathe and cut to suitable length (about 12 mm.). Other samples were cut with a jeweler's saw and trimmed with a file. They were weighed and loaded into a magazine which was placed into the side tube at the top of the apparatus. A nickel wire was loaded into the magazine after the last sample. The samples could thus be moved by means of a magnet and introduced onto a gate at the top of the apparatus, one at a time. The temperature at the gate was determined with a thermometer strapped to the tube with its bulb and the gate wrapped in oil-saturated cotton. The gate was placed at the top of the apparatus after it was demonstrated that some reaction took place when the gate was just above the calorimeter cup. The magazine and side tube were made of silica when it was desired to bake out the graphite at high temperature (1000°). Several specially designed bends were placed in the sample delivery tube to decrease the speed of delivery and thereby prevent splashing of potassium.

About 12 g. of potassium was distilled into the cup from an auxiliary vacuum system in the manner described in a previous article.[4] The analysis quoted there was for a sample used in the present work.

A copper–constantan thermocouple (#30 B & S gage wire) was welded to the platinum calorimeter cup. A piece of platinum sheet was placed over it and welded to the cup to prevent faulty temperature readings caused by heat conducted from the junction by the wires. The cold junction was attached to an aluminum shield surrounding the calorimeter tube and immersed in the thermostat. The couples were checked by placing one junction in an ice-bath while the other was in the thermostat. The couple was retained if the e.m.f. conformed within $^1/_2$% of the values given by Adams.[5]

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