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166. *Solutions in Sulphuric Acid. Part XXVI.* Cryoscopic Measurements by an Equilibrium Method.*

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An equilibrium method of measuring freezing points of solutions in sulphuric acid has been developed. The freezing points of solutions of water, disulphuric acid, lithium, sodium, potassium, ammonium, silver, and barium sulphates and benzophenone have been measured. The results differ appreciably from earlier results obtained by the Beckmann method, but agree with Kunzler and Giauque's equilibrium-method measurements on solutions of water and disulphuric acid. It is concluded that the present measurements are the most accurate and some of the possible errors in the earlier work are discussed.

ALMOST all previous cryoscopic measurements in sulphuric acid have been made by the Beckmann method.[1] Several errors, which are discussed below, are however possible in freezing points determined in this way and it was of interest to determine the freezing

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* Part XXV, *J.*, 1959, 2804.

[1] See, *e.g.*, Gillespie, Hughes, and Ingold, *J.*, 1950, 2473 and references therein.

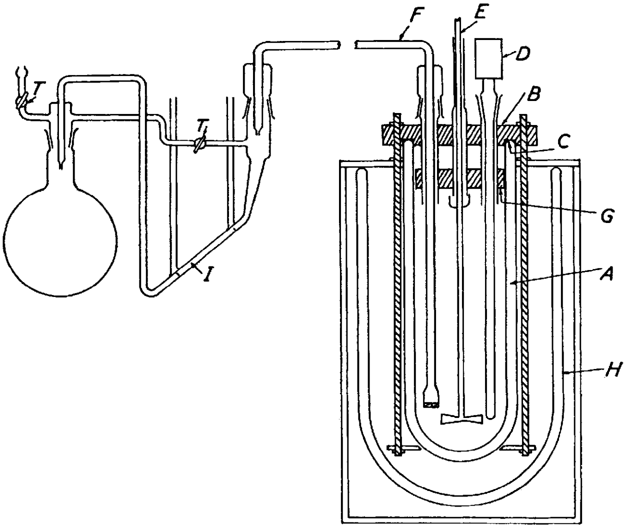
points of some solutions in sulphuric acid by the equilibrium method which is generally more reliable. Accurate values of the freezing points of electrolyte solutions in sulphuric acid were needed for the calculation of the osmotic coefficients of such solutions.[2]

In the equilibrium method a quantity of the solid solvent and solution are stirred together in a Dewar flask until a steady equilibrium temperature is obtained. A sample of the solution is then withdrawn and analysed. This technique has been used only once previously for sulphuric acid solutions, in the work of Kunzler and Giauque [3] with the solutes water and disulphuric acid. These authors determined the composition of the equilibrium liquid by direct chemical analysis in conjunction with a thermal method in which they calculated the liquid composition from a knowledge of the heat gained by the system and the appropriate values of the heat capacities and heat of fusion. In the present work a different method of analysis, namely, the determination of electrical conductivity at 25°, has been used and measurements have been made on other electrolytes in addition to water and disulphuric acid. This work became possible after the accurate conductivity measurements of various electrolyte solutions reported in a following paper [4] had been completed; the freezing-point measurements are, however, reported first since some of the conclusions that may be drawn from them are needed for a detailed interpretation of the conductivities.

EXPERIMENTAL

Apparatus.—The freezing-point measurements were made in a cryoscope (Fig. 1) constructed from a 10 × 30 cm. Dewar flask *A* fitted with a lid *B* made from ½″ Polythene sheet. A circular groove *C* cut in the bottom of the lid enabled it to fit snugly over the top of the Dewar flask. Four holes in the lid carried tightly fitting glass tubes with ground joints for the thermometer *D*, stirrer *E*, and withdrawal tube *F*, and for adding solutions for changing the composition. About 1 cm. below the lid *B* was a second Polythene lid *G* which fitted fairly tightly into the Dewar flask and had four similar holes for the thermometer, etc. This considerably improved the thermal insulation and minimised the leakage of atmospheric moisture into the cryoscope. Leakage of moisture was rendered quite negligible by maintaining a slight positive pressure of dry nitrogen in the space between the two lids. The Dewar flask *B* was supported inside a

FIG. 1. *Apparatus.*



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[2] Bass, Gillespie, Oubridge, and Robinson, following papers.

[3] Kunzler and Giauque, *J. Amer. Chem. Soc.*, 1952, **74**, 5271.

[4] Bass, Flowers and Gillespie, Part XXX, unpublished work.

larger Dewar flask *H* containing alcohol which could be cooled to any desired temperature, down to $-20°$, by a coil through which alcohol cooled by solid carbon dioxide was pumped. The stirrer *E* operated at approximately 120 r.p.m. At this and lower speeds the heat of stirring appeared to be very small and the temperature remained steady and independent of the rate of stirring. It was convenient, however, to be able to mix rapidly the whole after addition of solutions made to change the composition, by increasing the rate of stirring to about 800 r.p.m. for a few minutes.

Freezing points were measured with an N.P.L. calibrated platinum resistance thermometer which had a B.14 cone on its sheath and fitted into an appropriate socket on the lid *B*. The resistance of the thermometer was measured with a Cambridge Smiths difference bridge in conjunction with a galvanometer of sensitivity 150 mm./μ amp., on a scale at 1 m., and a Tinsley photoelectric galvanometer amplifier. The smallest change in resistance which could be detected was 10^{-5} ohm corresponding to a change in temperature of 0·0001°. The ice-point of the thermometer was checked from time to time throughout the work: a very slow drift was observed for which allowance was made.

Samples of solution for analysis were withdrawn through the tube *F* into the conductivity cell *I*, which was kept permanently connected to the cryoscope and was immersed in an oil thermostat[5] maintained at 25° ± 0·002°. The withdrawal tube *F* terminated in a sintered-glass disc in order to exclude solid crystals. The conductivity cell was filled by means of suction applied through drying tubes and manipulation of the taps *T*. In order to minimise the size of the sample taken for analysis the conductivity cell was made fairly small, being 10 cm. in length and 0·4 cm. in internal diameter. It sloped at approximately 45° to the vertical to prevent air bubbles collecting at the electrodes and to ensure good drainage when each sample was removed. The construction of the electrodes in the conductivity cell and the details of the apparatus used for the conductance measurements have been described previously.[5] The cell constant was determined by measuring the resistance of the cell containing sulphuric acid of minimum conductivity[5] ($\kappa = 0{\cdot}010433$ ohm^{-1} cm.$^{-1}$).

Materials.—Preparation of the sulphuric acid solvent has been previously described.[5] Its composition was adjusted to approximately 100% H_2SO_4 by addition of aqueous acid or oleum until its freezing point reached approximately the maximum value (10·371°). Final adjustment of the composition to 100% H_2SO_4 within $\pm 0{\cdot}0002$m (H_2O–$H_2S_2O_7$) was made in the cryoscope by following the conductivity which has the value[5] 0·010439 ohm^{-1} cm.$^{-1}$ at 100% H_2SO_4.

Potassium, lithium, and sodium sulphates were " AnalaR " reagents which had been dried at 500° and stored in a desiccator. " AnalaR " ammonium sulphate was dried over " Anhydrone " in a desiccator for two weeks. Silver sulphate was a commercial sample which was purified by dissolving it in hot concentrated sulphuric acid containing a trace of nitric acid. After cooling, the acid was diluted with water and the precipitated sulphate filtered off, washed, and dried at 120°. Barium sulphate was prepared by precipitation with sulphuric acid from an aqueous solution of " AnalaR " barium chloride, and dried at 500°. Benzophenone was a commercial sample twice recrystallised from ethanol and dried in a vacuum-desiccator.

Experimental Procedure.—About 1 l. of very nearly 100% sulphuric acid was cooled to $\sim 0°$ in a flask with stirring, and crystallisation was initiated by touching the outside of the flask with a small piece of solid carbon dioxide. The rapid crystallisation which ensued produced a convenient slurry of small crystals and liquid which was poured into the cryoscope through a funnel which fitted on to one of the tubes through the lid. The contents of the cryoscope were then stirred continuously until the temperature became steady and equilibrium between the solid and the solution had therefore presumably been reached. This temperature was recorded. Some of the solution was then drawn through the conductivity cell in order to wash it free from any moisture adsorbed on the walls, or, for later measurements, any residue from the previous sample. It was then filled with a sample for the conductivity measurement. The solution was allowed to remain in the conductivity cell for at least 10 min. in order to reach the temperature of the thermostat and its conductivity was then measured. The contents of the conductivity cell were withdrawn into the residue flask *J*. The temperature in the cryoscope was again recorded and the conductivity measured as before. In general, excellent agreement was obtained between measurements repeated in this manner. Final adjustment of the solvent composition to exactly 100% H_2SO_4 was made by adding small increments of aqueous acid or oleum until the minimum conductivity[5] ($\kappa = 0{\cdot}010433$ ohm^{-1} cm.$^{-1}$) was obtained and then

[5] Gillespie, Oubridge, and Solomons, *J.*, 1957, 1804.

adding the very small amount of oleum needed to obtain the 100% composition ($\kappa = 0{\cdot}010439$ ohm^{-1} cm.$^{-1}$). This careful adjustment of the composition of the acid was not, of course, necessary when the solutes were water and disulphuric acid. As most metal sulphates dissolve rather slowly in sulphuric acid at 10°, it was most convenient to prepare a fairly concentrated solution of these solutes in 100% H_2SO_4, and then add small amounts of this solution in order to change the composition. This solution was prepared by withdrawing a sample of the 100% acid from the cryoscope into a 250 c.c. conical flask containing some of the sulphate and dissolving the sulphate by gently warming and shaking. The flask was thereafter permanently connected to the cryoscope, and samples could be added to the cryoscope by applying a slight positive pressure of dry nitrogen. After each addition equilibrium was established, the temperature was recorded, and samples were withdrawn for conductivity measurements as described above. Because of the fairly large heat of solution of the electrolytes and the fact that the added electrolyte solution was at room temperature some of the solid acid was melted each time the composition was changed and there was generally insufficient solid to maintain equilibrium after a depression of about 4° had been obtained. If after the withdrawal of many samples of solution the level of the solution in the cryoscope became too low to give adequate immersion of the thermometer, a slurry of approximately 100% acid was added to restore the level in the case of the solutes water and disulphuric acid: with other solutes it was necessary to dismantle the apparatus and begin a new experiment.

RESULTS

Interpolated Freezing Points.—It is not practicable to give in detail the results of all the measurements. Table 1 gives interpolated values of the freezing points at round molal concentrations. For the solutes water and disulphuric acid values of the conductivities at round molal concentrations were obtained by interpolation from the large-scale plots used to obtain the data given in Part XXX.[4] From a plot of the thermometer resistance against the conductivity of the equilibrium liquid for a total of 150 different concentrations in eight separate experiments, values of the thermometer resistance at the conductivities corresponding to round molal concentrations were interpolated. A portion of this plot showing results from three experiments is shown in Fig. 2, which displays the good agreement and very small deviations.

TABLE 1. *Interpolated freezing points.*

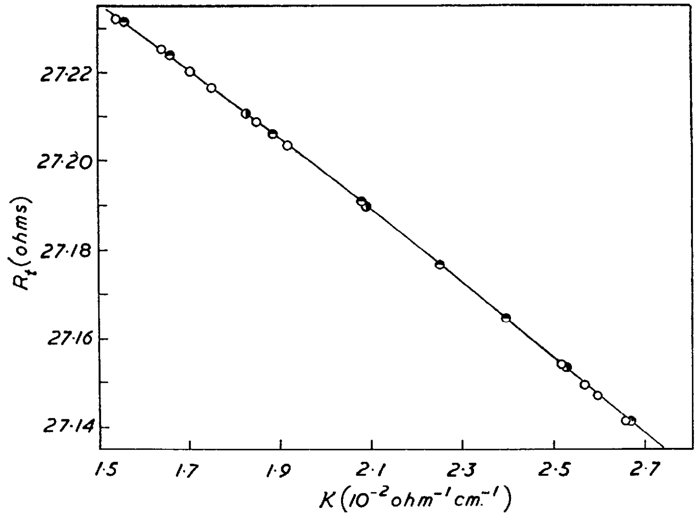
m	H_3O,HSO_4	$H_2S_2O_7$	$NaHSO_4$	$LiHSO_4$	$KHSO_4$	NH_4HSO_4	$AgHSO_4$	$Ph_2C(OH){\cdot}HSO_4$	$Ba(HSO_4)$
0·000	10·371°	10·371°	10·371°	10·371°	10·371°	10·371°	10·371°	10·371°	10·371°
0·005	10·364	10·366	10·339	10·339	10·339	10·339	—	—	—
0·010	10·346	10·351	10·300	10·301	10·301	10·302	—	—	10·275
0·015	10·316	10·329	10·258	10·260	10·260	10·261	—	—	—
0·020	10·280	10·305	10·213	10·214	10·214	10·215	—	—	10·136
0·025	10·237	10·276	10·163	10·165	10·165	10·166	—	—	—
0·030	10·194	10·248	10·113	10·115	10·115	10·117	10·118	10·105	9·965
0·035	10·146	10·214	10·061	10·062	10·062	10·067	10·067	10·050	—
0·040	10·094	10·182	10·006	10·009	10·009	10·015	10·018	9·994	9·775
0·050	9·993	10·118	9·895	9·902	9·902	9·905	9·915	9·878	9·581
0·060	9·885	10·049	9·779	9·785	9·785	9·793	9·806	9·762	9·386
0·070	9·783	9·980	9·664	9·670	9·670	9·679	9·699	9·638	9·191
0·080	9·674	9·912	9·546	9·555	9·555	9·566	9·590	9·517	8·994
0·090	9·564	9·843	9·427	9·435	9·435	9·447	9·480	9·386	8·795
0·100	9·453	9·773	9·304	9·316	9·316	9·332	9·370	9·260	8·588
0·120	9·241	9·673	9·056	9·074	9·079	9·100	9·151	8·995	—
0·140	9·024	9·500	8·798	8·831	8·836	8·866	8·930	8·723	—
0·160	8·807	9·366	8·543	8·582	8·590	8·632	8·712	8·447	—
0·180	8·591	9·229	8·283	8·336	8·345	8·400	8·494	8·164	—
0·200	8·375	9·095	8·022	8·092	8·101	8·166	8·280	7·877	—
0·220	8·168	8·960	7·756	7·838	7·848	7·932	8·066	7·590	—
0·240	7·956	8·821	7·485	7·577	7·600	7·695	7·855	7·280	—
0·260	7·745	8·689	7·212	7·318	—	—	7·642	—	—
0·280	7·537	8·550	6·948	—	—	—	7·432	—	—
0·320	7·130	8·281	—	—	—	—	—	—	—
0·360	6·725	—	—	—	—	—	—	—	—
0·400	6·324	—	—	—	—	—	—	—	—

Other methods of interpolation are possible and for the other electrolytes it was generally more convenient to determine the concentration of each sample of the equilibrium solution from its conductivity by interpolation from the conductivity–concentration plots used to obtain the data presented in Part XXX.[4] Then from the corresponding freezing points a plot of the freezing point against concentration was constructed and values of the freezing points were interpolated at round molal concentrations.

Accuracy of the Measurements.—The measurement of conductance, which could be made to 1 ohm in 10,000 (0·01%) was the most accurate part of the present work. The concentration–conductivity data that were used to obtain the corresponding concentrations involved relatively larger errors in the concentrations. These originate particularly from the difficulty of initially adjusting the composition of the solvent to 100% H_2SO_4, because the conductivity–concentration curve is very flat in this region.[5] Taking this and other factors into account we estimate that the errors in the concentrations are not greater than 0·0005m at 0·2m and rather less than this at lower concentrations. This corresponds to an error of ≯0·005° in the corresponding freezing points.

The measurement of the freezing points was not a serious source of error as these were made to 0·0002° at the lower concentrations and 0·001° at the higher concentrations. For all the electrolytes except water and disulphuric acid the difficulty of adjusting the acid initially to the composition 100% H_2SO_4 was also a source of error in the freezing-point measurements. The interpolations probably minimise the effects of random errors and therefore to some extent improve the accuracy. Taking all these factors into account and judging from the very small scatter of the experimental points in the plots made for obtaining the interpolated values (see Fig. 2) we estimate that the freezing points are accurate to 0·002° at concentrations up to 0·04m, to 0·005° up to 0·1m, and 0·01° up to 0·3m.

FIG. 2. *Plot of thermometer resistance against conductivity for solutions of water.*



○ ◑ ◓ *indicate different experiments.*

DISCUSSION

The Freezing Point of 100% H_2SO_4 *and the Composition of Minimum Conductance.*—The maximum freezing point at the composition 100% H_2SO_4 was determined many times and was found to be 10·371°. This is higher than the value of 10·365° obtained by Gillespie and Oubridge[6] by the Beckmann method, but it is in exact agreement with the value obtained by Kunzler and Giauque[3] by their equilibrium method. The composition of minimum conductance was determined many times and found to be 0·0019 ± 0·005 mole of H_2O per kg. of solution, as found by Gillespie, Oubridge, and Solomons.[5]

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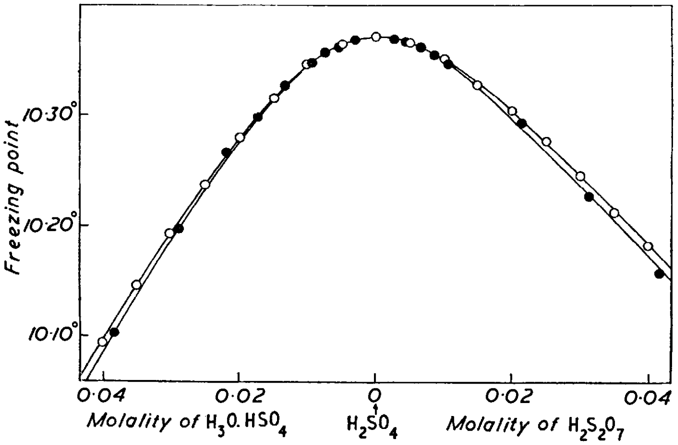
[6] Gillespie and Oubridge, *J.*, 1956, 80.

Comparison with the Work of Kunzler and Giauque.—For solutions of water and disulphuric acid Kunzler and Giauque [3] reported lower freezing points than ours for all concentrations except in the immediate vicinity of the maximum freezing point (see Fig. 3). The differences increase with increasing concentration and become as large as 0·03° at 99·8% H_2SO_4 [= 0·1m(H_2O)]. Such differences are outside the possible error in our measurements. Most of Kunzler and Giauque's determinations up to this concentration depend on the analysis of one solution at 99·8% H_2SO_4, for which they estimated that the error in the composition was ±0·005%, which is equivalent to 0·03°, the possible error at lower concentrations being proportionally smaller. Their results can be brought into concordance with ours if it is assumed that their analytical error at 99·8% H_2SO_4 was —0·005% —0·003m(H_2O)]. If their concentrations are all corrected on this basis, the error at other concentrations being taken as proportional to the concentration, their freezing points are found to be in satisfactory agreement with ours.

FIG. 3. *Comparison of freezing points in the region of the maximum at the composition* H_2SO_4 *with Kunzler and Giauque's results.*



● *Kunzler and Giauque.*[3] ○ *Present work.*

Possible Errors of the Equilibrium Method.—The validity of the equilibrium method depends on establishment of equilibrium between the solid phase and the solution. However, heat will leak into the cryoscope through the lid and will be generated by the stirrer, while it may leak out of the cryoscope through its walls. As a consequence there will in general be a small overall gain or loss of heat. This means that true equilibrium is probably never established. There will be a slow freezing out or melting of the solid phase and thus the liquid in the immediate vicinity of the crystals will not have the same composition as that of the bulk liquid, so that the measured freezing point will be slightly different from the true equilibrium temperature. However, non-equilibration in the present experiments must have been very slight since the temperature only drifted one or two thousandths of a degree in several hours once " equilibrium " had been established. Moreover good agreement was always obtained between the results of different experiments (see Fig. 2): if equilibrium had not been quite closely attained, the different conditions, *e.g.*, different room temperatures and different relative amounts of the solid and liquid phases, would have been expected to lead to measurable differences between the results of these experiments.

It is also important that the solid phase should have exactly the composition 100% H_2SO_4. That this is so within a few thousandths of a percent has been shown by Kunzler and Giauque [3] for the equilibrium solid. It is also possible that a non-equilibrium solid containing molecules and/or ions of H_2O or $H_2S_2O_7$ might be obtained. In the preparation of the required slurry of solid and liquid, however, the composition of the acid used was always very close to 100%; its freezing point was always within a few hundredths of a degree of the maximum value. Thus the concentration of any such non-equilibrium component of the solid phase could only be very small. Again the good agreement between the results of different experiments suggests that any error from this source, which would be likely to differ from one experiment to another, is probably very small.

Another possible source of error could be that very small crystals of the solid phase passed through the sintered-glass disc at the end of the withdrawal tube when samples were removed for the determination of their conductivities. This would not, however, account for our freezing points' being higher than Kunzler and Giauque's. It would be expected to lead to random differences between repeated measurements of the conductivity of different samples of the same solution and to random differences between the results of different experiments. Again the reproducibility of the results suggests that any error from this source must be very small.

Comparison with the Beckmann method.—A considerable amount of work on the freezing points of solutions in sulphuric acid has been carried out by the Beckmann method.[1] In Gillespie and Oubridge's work [6] an attempt was made to use this method to obtain freezing points of solutions of some simple electrolytes, *e.g.*, metal sulphates, with sufficient accuracy to enable osmotic coefficients to be calculated. However, the freezing points obtained in the present work are in all cases appreciably higher than theirs for all the metal sulphates investigated (cf. Table 2), and they are also higher than the freezing points obtained by Gillespie [7] for the solutes water and disulphuric acid.

TABLE 2. *Comparison of freezing points obtained by the Beckmann and the equilibrium method.*

10^3 [Temp. (equil.) − Temp. (Beckmann)].

m	$LiHSO_4$	$NaHSO_4$	$KHSO_4$	NH_4HSO_4	$AgHSO_4$
0·02	11°	13°	11°	10°	—
0·04	19	21	19	20	16°
0·06	28	34	28	29	26
0·08	35	41	35	26	34
0·10	35	46	39	22	40
0·12	41	54	47	25	49
0·14	49	56	58	33	43
0·16	47	61	65	37	67
0·18	56	62	74	45	70
0·20	55	67	81	47	80

Thus it appears that there are appreciable errors in freezing points determined by the Beckmann method.

A possible source of error in the Bechmann method is the supercooling correction which is applied to allow for the change in the composition of the solution due to the solid solvent which separates on freezing. In the expression given [1] for this correction, allowance was made for the heat capacity of the solution and the solid solvent, but not for that of the cryoscope and for any heat lost to the surroundings, and these are not negligible. Nevertheless any error in the supercooling correction is certainly not large enough to account for the whole of any of the differences observed.

Another error in the Beckmann method arises because proper equilibrium between the solid and the liquid is not, in general, established. Under the usual conditions of the method the external bath-temperature is lower than that of the solution in the cryoscope and solid is continually freezing out, so that if the rate of crystallisation is not sufficiently rapid the liquid will be at a slightly lower temperature than the true equilibrium freezing-point.

Because the rate of crystallisation of the supercooled solution is rather rapid it is possible that a non-equilibrium solid is formed containing a small amount of the solute.

[7] Gillespie, *J.*, 1950, 2493.

This also could lead to observed temperatures lower than the true equilibrium freezing point; it could account too for the fact that the differences between the freezing points determined by the Beckmann method and by the equilibrium method vary from one solute to another (see Table 2), as the composition of any non-equilibrium solid might reasonably depend on the nature of the electrolyte—the size of the ions of the electrolyte would, for example, determine the ease with which they could be accommodated in the lattice of solid sulphuric acid.

The errors that appear to exist in freezing points of sulphuric acid solutions determined by the Beckmann method are, however, not large enough to affect the general conclusions reached in previous Parts of this series concerning the mode and approximate degree of ionisation of various solutes in sulphuric acid. In view of the simplicity of the Beckmann method, and the ease and speed with which measurements can be made, it is still very useful when the highest accuracy is not required. The technique can probably be modified so as to minimise some of the errors discussed above and thus to improve the accuracy of the method.

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