# **130.** *Solutions in Sulphuric Acid. Part XXIV.* Electrical Conductivity, Cryoscopic, and Density Measurements on Solutions in Dideuterosulphuric Acid.*

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Freezing points, and the densities and electrical conductivities at 25°, of the system $D_2O-SO_3$ have been measured in the region of the composition $D_2SO_4$ and of solutions of $KDSO_4$ and $NaDSO_4$ in 100% $D_2SO_4$. Some conductivities of the $D_2O-SO_3$ system and of solutions of $KDSO_4$ were also measured at 10° and 40°. The freezing point of $D_2SO_4$ is 14·35° ± 0·02°, its cryoscopic constant is 6·5, its specific conductance is $2{\cdot}568 \times 10^{-3}$ ohm$^{-1}$ cm.$^{-1}$, and its density ($d_4^{25}$) is 1·8573. From the results of the cryoscopic measurements the extent of self-dissociation of the solvent, and equilibrium constants for the reaction of $D_2O$ and $D_2S_2O_7$ with the solvent have been calculated. The degree of ionisation of *m*-nitrotoluene in $D_2SO_4$ was also investigated.

The ions $H_3SO_4^+$ and $HSO_4^-$ produced by the ionisation of acids and bases, respectively, in sulphuric acid have very abnormally high mobilities because they conduct by a proton-transfer mechanism. Although the general nature of the proton-transfer conduction process is clear, many of its details are still obscure. Some of the factors determining the rate of this conduction process were discussed in Part XII;[1] it involves proton transfer from an ion to a solvent molecule or *vice versa* and probably some orientation process involving ions and/or solvent molecules. It was with the hope of improving our knowledge of the mechanism of electrical conduction in sulphuric acid that the present measurement were made. In addition to conductivity measurements on solutions of $D_2O$, $SO_3$, $KDSO_4$, and $NaDSO_4$ in dideuterosulphuric acid it was necessary to determine freezing points and densities of the same solutions in order to obtain information necessary to interpret the conductivity results. The calculation and discussion of the mobilities of the ions $D_3SO_4^+$ and $DSO_4^-$ is deferred.

## Experimental

*Apparatus.*—The apparatus used for the freezing point and conductivity measurements has been described previously.[2, 3a] The densities of a few solutions were measured with a 10 c.c. specific gravity bottle. Most of the density measurements were made by a float method in the apparatus shown in Fig. 1. It was permanently attached to a conductivity cell and filled from the cell by suction. Thus the density of every solution whose conductivity was measured could be found quickly and conveniently without exposing the solution to the atmosphere. This densitometer consisted of a vertical tube (*A*), 1·5 cm. in diameter, around whose upper part was wound a solenoid (*B*) consisting of 6000 turns of 36 s.w.g. enamelled copper wire. The float (*C*) was a thin-walled glass cylinder of length 10 cm. and diameter 0·5 cm. This was made to float upright by means of an iron pellet sealed into the lower end. A small piece of soft iron (*D*) was sealed into the upper end. The float had four sharp glass spikes (*E*) protruding from its lower end, in order to prevent the main body of the float from coming into contact with the walls of the float chamber; otherwise the effects of surface tension were serious. A small platinum point (*F*) was mounted in the lower part of the tube and when this was empty or when it contained a solution of sufficiently low density the flat bottom of the float rested on this point. The weight of the float could be adjusted by small rings of platinum wire (*G*) so that it sank in those solutions whose densities were to be measured. After the densitometer had been filled with such a solution, the current through the solenoid was adjusted until it was just sufficient to raise the float from the platinum point. This was repeated several times for each

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* Part XXIII, Gillespie and Robinson, *J.*, 1957, 4233.

[1] Gillespie and Wasif, *J.*, 1953, 221.

[2] Gillespie, Hughes, and Ingold, *J.*, 1950, 2475.

[3] (*a*) Gillespie, Oubridge, and Solomons, *J.*, 1957, 1804; (*b*) Kunzler and Giauque, *J. Amer. Chem. Soc.*, 1952, **74**, 804.

solution, the float being observed by means of a telescope mounted outside a glass panel in the side of the water thermostat (at 25° ± 0·005°) in which the combined conductance cell-densitometer was suspended. The current through the solenoid was measured on a milliammeter reading up to 150 mA with an accuracy of 1 mA. The densitometer had a range of 0·02 g. cm.$^{-3}$ for any given weight on the float, and an accuracy of ±0·0002 g. cm.$^{-3}$. A calibration curve showing the relation between the current and the density was obtained (i) by using solutions of potassium sulphate in sulphuric acid whose densities had been accurately measured by using the 10 c.c. specific gravity bottle and (ii) by successively adding to the float small platinum rings weighing about 0·01 g. each and observing the current needed to raise the float after each addition. The agreement between the two methods was satisfactory. The instrument was re-calibrated periodically, but no significant changes were observed.

*Dideuterosulphuric Acid.*—Sulphur trioxide, prepared and purified as described previously,[3] was distilled slowly into deuterium oxide (Norske Hydro 99·97% $D_2O$), the reaction vessel being cooled in an ice–salt bath. The reaction is vigorous, but not violent, below 0°. The composition of the product was found approximately from the weight of deuterium oxide taken and the weight of acid formed.

FIG. 1. *Densitometer.*

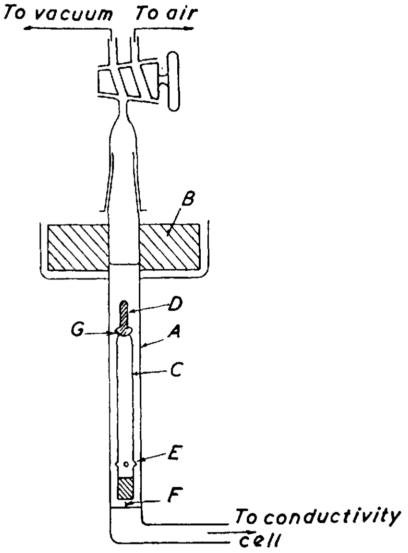
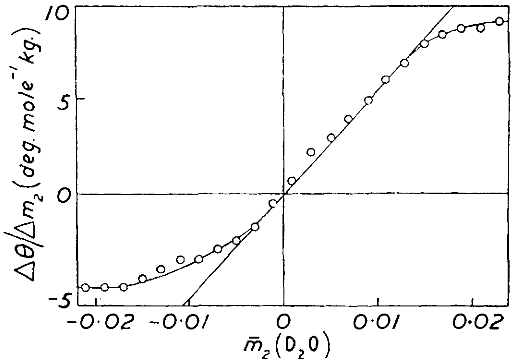


FIG. 2. *Plot for determining the degree of dissociation of* $D_2SO_4$.



*Potassium and Sodium Sulphates.*—" AnalaR " salts were dried at 150° for 2 hr. and stored in a desiccator over phosphoric oxide.

*Experimental Procedure.*—The combined conductivity–freezing-point measurements on the $D_2O$–$SO_3$ system were carried out as for the $H_2O$–$SO_3$ system.[3] For the conductivity measurements on solutions of $K_2SO_4$ and $Na_2SO_4$ the solvent was initially adjusted to the composition 100% $D_2SO_4$ by making small additions of a dilute solution of $D_2O$ in $D_2SO_4$ to a dilute oleum until it had the correct conductivity. Successive weighed portions of $K_2SO_4$ or $Na_2SO_4$ were then added to the solvent and the conductivity was measured. The freezing-point measurements on solutions of $K_2SO_4$ were made as previously described[4] after initially adjusting the solvent to maximum freezing point.

*Results.*—It is not possible to give all our many results in detail. The results of the measurements of the freezing point and of the conductivity at 25° in the immediate neighbourhood of the composition $D_2SO_4$ are shown graphically in Fig. 2. From a large-scale version of this plot and others covering larger concentration ranges, values of specific conductance and of freezing point were interpolated at round concentrations. These values are given in Tables 1 and 2, together with similar values for solutions of $KDSO_4$ and $NaDSO_4$.

The maximum freezing point, *i.e.*, the freezing point of $D_2SO_4$, is 14·35 ± 0·02°. The freezing point of $H_2SO_4$ is 10·37°. The error given is an estimate of the absolute error of the

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

measurements; the relative error was smaller and the maximum freezing point was generally found to be within a few thousandths of a degree of 14·347°; hence this is the value given in the Tables and used in the calculations. Fig. 2 shows that the minimum conductivity occurs on the oleum side of the composition $D_2SO_4$ and not on the aqueous side [3] as for $H_2SO_4$. The values of the composition of minimum conductivity at 25° and of the specific conductance at this composition and at 100% $D_2SO_4$ are given in Table 3. A few rather less accurate observations were made at 10° and 40° in the immediate neighbourhood of the composition $D_2SO_4$. The values of the specific conductance at this composition at the temperatures 10° and 40° are also given in Table 3. The results of the measurements of the conductivities of solutions of $KDSO_4$ at 10° and 40° are given in Table 4 together with values of the ratio $\kappa_{25°}/\kappa_{10°}$ which are needed in a following paper.

TABLE 1. *Interpolated freezing points of solutions in dideuterosulphuric acid.*

| Concn. (m) | $D_2S_2O_7$ | $D_2O$ | $KDSO_4$ | Concn. (m) | $D_2S_2O_7$ | $D_2O$ | $KDSO_4$ | Concn. (m) | $D_2S_2O_7$ |
|---|---|---|---|---|---|---|---|---|---|
| 0·0000 | 14·347° | 14·347° | 14·347° | 0·0400 | 14·170° | 14·025° | 13·925° | 0·2000 | 13·100° |
| 0·0050 | 14·340 | 14·338 | — | 0·0600 | 14·044 | 13·803 | 13·681 | 0·2400 | 12·824 |
| 0·0100 | 14·325 | 14·317 | 14·263 | 0·0800 | 13·910 | 13·578 | 13·425 | 0·2800 | 12·550 |
| 0·0150 | 14·306 | 14·283 | — | 0·1000 | 13·777 | 13·352 | 13·173 | | |
| 0·0200 | 14·282 | 14·240 | 14·163 | 0·1200 | 13·645 | 13·135 | 12·916 | | |
| 0·0250 | 14·256 | 14·194 | — | 0·1450 | 13·508 | 12·920 | 12·660 | | |
| 0·0300 | 14·228 | 14·149 | 14·020 | 0·1600 | 13·370 | — | 12·401 | | |

TABLE 2. *Interpolated specific conductances of solutions in dideuterosulphuric acid at* 25°.

| Concn. | $\kappa$ ($10^{-2}$ ohm$^{-1}$ cm.$^{-1}$) | | | | Concn. | $\kappa$ ($10^{-2}$ ohm$^{-1}$ cm.$^{-1}$) | | | |
|---|---|---|---|---|---|---|---|---|---|
| (mole $kg._{soln.}^{-1}$) | $D_2O$ | $D_2S_2O_7$ | $KDSO_4$ | $NaDSO_4$ | (mole $kg._{soln.}^{-1}$) | $D_2O$ | $D_2S_2O_7$ | $KDSO_4$ | $NaDSO_4$ |
| 0·000 | 0·2568 | 0·2568 | 0·2568 | 0·2568 | 0·08 | 0·898 | 0·403 | 0·940 | 0·912 |
| 0·002 | 0·2596 | 0·2546 | — | — | 0·09 | 0·988 | 0·423 | 1·033 | 1·003 |
| 0·004 | 0·2645 | 0·2541 | — | — | 0·10 | 1·075 | 0·443 | 1·124 | 1·100 |
| 0·006 | 0·2700 | 0·2542 | — | — | 0·12 | 1·251 | 0·479 | 1·310 | 1·264 |
| 0·008 | 0·2775 | 0·2553 | — | — | 0·14 | 1·421 | 0·511 | 1·487 | 1·480 |
| 0·010 | 0·2862 | 0·2572 | 0·300 | 0·300 | 0·16 | 1·587 | 0·543 | 1·660 | 1·591 |
| 0·015 | 0·3130 | 0·2640 | 0·326 | 0·326 | 0·18 | 1·750 | 0·574 | 1·829 | 1·742 |
| 0·020 | 0·345 | 0·272 | 0·368 | 0·368 | 0·20 | 1·91 | 0·603 | 1·99 | 1·89 |
| 0·025 | 0·378 | 0·282 | 0·405 | 0·405 | 0·25 | 2·30 | 0·670 | 2·37 | 2·23 |
| 0·03 | 0·420 | 0·292 | 0·452 | 0·452 | 0·30 | 2·65 | 0·727 | 2·73 | 2·54 |
| 0·04 | 0·518 | 0·316 | 0·549 | 0·547 | 0·35 | 2·98 | 0·779 | 3·06 | 2·82 |
| 0·05 | 0·616 | 0·337 | 0·642 | 0·639 | 0·40 | 3·29 | 0·827 | 3·37 | 3·07 |
| 0·06 | 0·711 | 0·378 | 0·740 | 0·733 | 0·45 | 3·58 | 0·870 | 3·65 | 3·29 |
| 0·07 | 0·807 | 0·381 | 0·835 | 0·823 | 0·50 | 3·85 | 0·909 | 3·91 | 3·51 |

TABLE 3. *Specific conductances at the composition* $D_2SO_4$ *and at the composition of minimum conductance.*

| Temp. | $\kappa$ ($10^{-2}$ ohm$^{-1}$ cm.$^{-1}$) $D_2SO_4$ | $\kappa$ ($10^{-2}$ ohm$^{-1}$ cm.$^{-1}$) " Minimum " | Composition at minimum conductance (moles of $D_2S_2O_7$ $kg._{soln.}^{-1}$) |
|---|---|---|---|
| 10·0° | 0·133 ± 0·001 | — | — |
| 25·0 | 0·2568 ± 0·0005 | 0·2540 ± 0·0005 | 0·0045 ± 0·001 |
| 40·0 | 0·446 ± 0·001 | — | — |

TABLE 4. *Interpolated specific conductances of solutions of potassium deuterium sulphate at* 10° *and* 40°.

| Concn. | $\kappa$ ($10^{-2}$ ohm$^{-1}$ cm.$^{-1}$) | | | Concn. | $\kappa$ ($10^{-2}$ ohm$^{-1}$ cm.$^{-1}$) | | |
|---|---|---|---|---|---|---|---|
| (mole $kg._{soln.}^{-1}$) | 10° | 40° | $\kappa_{25°}/\kappa_{10°}$ | (mole $kg._{soln.}^{-1}$) | 10° | 40° | $\kappa_{25°}/\kappa_{10°}$ |
| 0·00 | 0·133 | 0·448 | 1·93 | 0·12 | 0·854 | 1·91 | 1·53 |
| 0·02 | 0·220 | 0·600 | 1·67 | 0·14 | 0·977 | 2·18 | 1·53 |
| 0·04 | 0·346 | 0·847 | 1·58 | 0·16 | 1·08 | 2·43 | 1·54 |
| 0·06 | 0·474 | 1·11 | 1·56 | 0·18 | 1·19 | 2·67 | 1·54 |
| 0·08 | 0·601 | 1·37 | 1·56 | 0·20 | 1·30 | 2·89 | 1·53 |
| 0·10 | 0·727 | 1·64 | 1·54 | | | | |

Interpolated values of the densities of solutions of $D_2O$, $D_2S_2O_7$, $KDSO_4$, and $NaDSO_4$ at 25° are given in Table 5.

TABLE 5. *Interpolated densities of solutions in dideuterosulphuric acid at 25°.*

| Concn. (mole $kg._{soln.}^{-1}$) | $d_4^{25}$ $D_2O$ | $d_4^{25}$ $D_2S_2O_7$ | $d_4^{25}$ $KDSO_4$ | $d_4^{25}$ $NaDSO_4$ |
|---|---|---|---|---|
| 0·00 | 1·8573 | 1·8573 | 1·8573 | 1·8573 |
| 0·02 | 1·8574 | 1·8576 | 1·8583 | 1·8582 |
| 0·04 | 1·8575 | 1·8580 | 1·8597 | 1·8595 |
| 0·06 | 1·8576 | 1·8585 | 1·8610 | 1·8607 |
| 0·08 | 1·8577 | 1·8588 | 1·8624 | 1·8620 |
| 0·10 | 1·8578 | 1·8692 | 1·8637 | 1·8632 |
| 0·15 | 1·8580 | 1·8604 | 1·8672 | 1·8663 |
| 0·20 | 1·8582 | 1·8615 | 1·8707 | 1·8694 |
| 0·25 | | 1·8628 | 1·8742 | 1·8726 |
| 0·30 | | 1·8642 | 1·8778 | 1·8757 |
| 0·35 | | 1·8654 | 1·8813 | 1·8789 |
| 0·40 | | 1·8668 | 1·8850 | 1·8821 |
| 0·45 | | 1·8682 | 1·8886 | 1·8853 |
| 0·50 | | 1·8695 | 1·8922 | 1·8888 |
| 0·60 | | 1·8721 | 1·8993 | 1·8950 |

## DISCUSSION

*The Self-dissociation of Dideuterosulphuric Acid: Preliminary Estimate.*—Dideuterosulphuric acid self-dissociates in the same way as sulphuric acid [5] according to the equation

$$2D_2SO_4 = D_2O + D_2S_2O_7 \quad . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

As shown later, $D_2O$ is extensively ionised according to the equation

$$D_2O + D_2SO_4 = D_3O^+ + DSO_4^- \quad . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

but $D_2S_2O_7$ is only slightly ionised. The overall dissociation reaction can therefore be written to a good approximation as

$$3D_2SO_4 = D_3O^+ + DSO_4^- + D_2S_2O_7 \quad . \; . \; . \; . \; . \; . \; . \quad (3)$$

According to Wyatt [6] the extent of dissociation $\alpha$ of a solvent dissociating according to the equation

$$nC = A(\longrightarrow a \text{ particles}) + B(\longrightarrow b \text{ particles})$$

is

$$\alpha = -k_f\, abn/(a + b)m_1\, (\partial^2 T/\partial m_2^{\,2})_{m_2=0} \quad . \; . \; . \; . \; . \; . \quad (4)$$

For the dissociation given in eqn. (3), $a = 2$, $b = 1$, and $n = 3$, hence eqn. (4) becomes

$$a = -2\, k_f/m_1\, (\partial^2 T/\partial m_2^{\,2})_{m_2=0} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (5)$$

where $k_f$ is the cryoscopic constant of the solvent, $m_1$ the molality of the solvent, $m_2$ the molality of the solute, and $T$ the freezing point. The value of $(\partial^2 T/\partial m_2^{\,2})_{m_2=0}$ can be found by plotting $\Delta\theta/\Delta m_2 = -\Delta T/\Delta m_2$ against $\overline{m_2}$. This has been done with the freezing points given in Fig. 2, and the resulting plot is shown in Fig. 3. The slope at $m_2 = 0$, *i.e.*, $(\partial^2 T/\partial m_2^{\,2})_{m_2=0}$ is $-5{\cdot}5 \times 10^2$ deg. kg.$^2$ mole$^{-2}$. Hence from eqn. (5), taking $k_f = 6{\cdot}5$ (p. 672), we find that $\alpha = 2{\cdot}4 \times 10^{-3}$. Hence the total concentration of dissociation products, $m_\alpha$, is 0·024m, and therefore

$$[D_3O^+] = [D_2S_2O_7] = [DSO_4^-] = 8 \times 10^{-3}\text{m}$$

Thus

$$K_d = [D_3O^+][DSO_4^-][D_2S_2O_7] = 5{\cdot}1 \times 10^{-7} \text{ mole}^3 \text{ kg.}^{-3}$$

The total depression of the freezing point produced by the products of the self-dissociation is given by $\delta = k_f m_d = 0{\cdot}155°$. Hence, if the self-dissociation can be represented by eqn. (3), the theoretical freezing point of the hypothetical undissociated acid is $T_0{}' = 14{\cdot}50_3°$.

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[5] Gillespie, *J.*, 1950, 2516.

[6] Wyatt, *Trans. Faraday Soc.*, 1956, **52**, 806.

*The Cryoscopic Constant and the Heat of Fusion.*—A value for the cryoscopic constant of dideuterosulphuric acid can be obtained from the results of our measurements on the freezing points of solutions of potassium sulphate, which may be assumed to be fully ionised, by assuming that the deviations from ideal behaviour in solutions of $K_2SO_4$ in $D_2SO_4$ are the same as in solutions of $K_2SO_4$ in $H_2SO_4$ at the same ionic strength.

The general equation [4] relating the freezing-point depression $\theta$ to the molality $m_2$ of the solute is

$$\theta/m_2 = g\nu k_f\{1 - (1/T_0 - \Delta C_p/2\Delta H_0^f)\theta\}\{1 + (2s - \nu)m_2/2m_1\} \quad . \quad . \quad (6)$$

where $\nu$ is the number of moles of ions and molecules formed in solution by one mole of the solute, $k_f$ is the cryoscopic constant, $g$ is the osmotic coefficient, $T_0$ is the freezing point of the pure solvent, $\Delta C_p$ is the difference between the heat capacities of the solid and the liquid solvent, $\Delta H_0^f$ is the heat of fusion of the pure solvent, and $s$ is the number of moles of solvent required to react with one mole of the solute. If we assume that $\Delta C_p$ and $\Delta H_0^f$ have the same value as for $H_2SO_4$, which is very likely to be a reasonably good approximation and will not therefore cause any error because $(1/T_0 - \Delta C_p/2\Delta H_0^f)\theta \ll 1$, we obtain a value of 0·0018 for the term $(1/T_0 - \Delta C_p/2\Delta H_0^f)$. Since $K_2SO_4$ ionises according to the equation

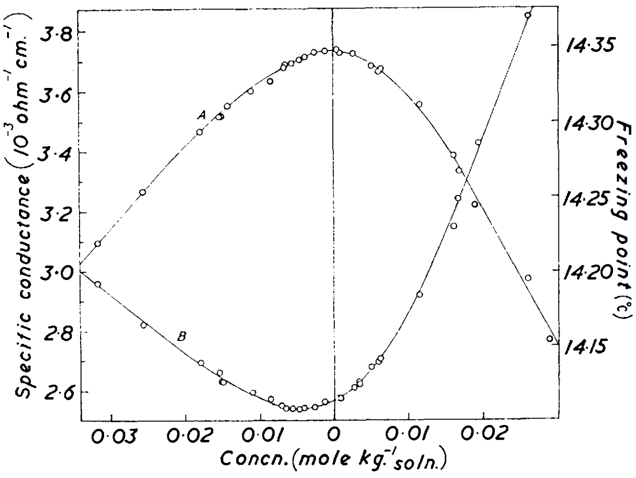

FIG. 3. *Freezing points and specific conductances in the region of the composition* $D_2SO_4$.
Curve *A*: Freezing-point depression.
Curve *B*: Specific conductance.

$$K_2SO_4 + D_2SO_4 = 2K^+ + 2DSO_4^-$$

we have $s = 1$ and $\nu = 4$, and since also $m_1 = 9·99$ we can write

$$\theta/m_2 = 4gk_f(1 - 0·0018\theta)(1 - m_2/9·99) \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Now if we substitute for $\theta$, $m_2$, and $g$, using values of $g$ for solutions of $K_2SO_4$ in $H_2SO_4$ at the same total ionic strength (allowing for the contribution of the self-dissociation products), we obtain the values of $k_f$ given in Table 6 and hence the mean value $k_f = 6·47$ deg. mole$^{-1}$ kg. The accuracy of this value is difficult to assess because the reliability of the method by which it was obtained is uncertain. It seems probable, however, that $k_f = 6·5 \pm 0·1$ deg. mole$^{-1}$ kg. By substituting for $T_0$, $\boldsymbol{R}$, and $m_1$ in the equation

$$k_f = \boldsymbol{R}T_0^2/m_1\Delta H_0^f$$

we obtain the value of 2540 calories for the heat of fusion ($\Delta H_0^f$) of dideuterosulphuric acid. Within the rather uncertain accuracy of the above method of determining this quantity it cannot be said to differ significantly from the heat of fusion of $H_2SO_4$ ($\Delta H_0^f$ = 2560 cal. mole$^{-1}$).

Some calorimetric measurements were also made which showed within a rather large experimental error that the heats of fusion of $H_2SO_4$ and $D_2SO_4$ are approximately the same. The method used was to drop a sample of the acid ($H_2SO_4$ or $D_2SO_4$) in a sealed tube at 0° into a calorimeter consisting of a Dewar flask containing water, and to observe the decrease in temperature that this produced. Owing to relatively large errors in cooling corrections the results were not of sufficient accuracy to warrant their detailed presentation.

The cryoscopic constants of $H_2SO_4$ and $D_2SO_4$ thus appear to differ not because of any appreciable difference in their heats of fusion but because of their different freezing points and molecular weights.

TABLE 6. *Calculation of the cryoscopic constant.*

| Concn. (m) $KDSO_4$ | F. p. (obs.) | F. p.* (corr.) | $\theta$ | $gk_f$ | $\mu^{\frac{1}{2}}$ | $g$ | $k_f$ | |
|---|---|---|---|---|---|---|---|---|
| 0·00 | 14·347° | 14·502° | — | — | — | — | — | |
| 0·02 | 14·160 | 14·248 | 0·254° | 6·34 | 0·1549 | 0·982 | 6·47 | Mean, 6·47 |
| 0·04 | 13·922 | 13·989 | 0·513 | 6·43 | 0·2073 | 0·985 | 6·53 | |
| 0·06 | 13·678 | 13·732 | 0·770 | 6·44 | 0·2510 | 0·991 | 6·50 | |
| 0·08 | 13·422 | 13·468 | 1·034 | 6·49 | 0·2863 | 0·997 | 6·51 | |
| 0·10 | 13·170 | 13·212 | 1·290 | 6·49 | 0·3193 | 1·002 | 6·48 | |
| 0·12 | 12·913 | 12·951 | 1·551 | 6·51 | 0·3493 | 1·009 | 6·46 | |
| 0·14 | 12·657 | 12·691 | 1·811 | 6·53 | 0·3770 | 1·015 | 6·43 | |
| 0·16 | 12·398 | 12·430 | 2·072 | 6·55 | 0·4025 | 1·022 | 6·42 | |

* The observed freezing points corrected for the depression due to the products of the self-dissociation of the solvent, by use of $K_d = 5{\cdot}1 \times 10^{-7}$. The depressions $\theta$ were calculated from these corrected freezing points.

*The Basic Strength of Deuterium Oxide.*—Deuterium oxide is extensively but apparently not completely ionised according to the equation

$$D_2O + D_2SO_4 = D_3O^+ + DSO_4^-$$

The calculation of the basicity constant $K_b(D_2O) = [D_3O^+][DSO_4^-]/[D_2O]$ is set out in Table 7. Column 1 gives the molality of $D_2O$, and column 2 the observed freezing points. These have been corrected for the freezing-point depression produced by the products of self-dissociation by using the constant $K_d = 5{\cdot}1 \times 10^{-7}$ and the corrected values are given in column 3. The depressions $\theta$ were calculated from these values. If we set $s = 1$ and $\nu \sim 2$ [see eqn. (2)] in the final term of eqn. (6) it reduces to

$$\theta/m_2 = g\nu k_f(1 - 0{\cdot}0018\theta) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

from which the values of $g\nu$ were calculated. The necessary estimates for $g$ were made by taking the values [4] for $K_2SO_4$ in $H_2SO_4$ at the same total ionic strength, $D_2O$ being assumed fully ionised. This assumption was made in order to make some allowance for the effect of the un-ionised part of the $D_2O$ on the osmotic coefficient $g$, which, because it is undoubtedly solvated by forming hydrogen bonds with solvent molecules, might be expected to be similar in its effect to $D_3O^+$ at the relatively high concentrations with which we are concerned. These values of $g$ are given in column 6. Hence the values of $\nu$ were obtained. Finally $K_b$ was calculated from the expression

$$K_b = (\nu - 1)[DSO_4^-]/(2 - \nu)$$

The mean value is $K_b = 0{\cdot}23$.

*The Acid Strength of Dideuterodisulphuric Acid.*—The calculation of the acid dissociation constant of dideuterodisulphuric acid is set out in Table 8. No adequate allowance can be made for non-ideality in this case so the osmotic coefficient $g$ was set equal to unity at all concentrations. The assumption made previously that the dideuterodisulphuric acid produced in 100% acid by the self-ionisation reaction is not ionised is not a sufficiently good approximation for solutions of dideuterodisulphuric acid, the self-dissociation being, in fact, repressed to a greater extent than this assumption would predict. Owing to the difficulty of allowing adequately for the repression of the self-dissociation, values of $\nu$, and hence of $K_a$, have only been calculated for concentrations of 0·08m and greater, for which it is certain that the self-dissociation is more than 70% repressed, and they have been calculated by assuming that the self-dissociation is completely repressed. The acid dissociation constant $K_a$ was calculated from the expression $K_a = (\nu - 1)^2 m/(2 - \nu)$ and the approximate constancy of the value obtained suggests that the various assumptions and approximations on which the calculation is based are reasonably valid. The mean value of $K_a = 2 \times 10^{-3}$ shows that dideuterodisulphuric acid is an appreciably weaker acid in $D_2SO_4$ than disulphuric acid ($K_a = 2 \times 10^{-2}$) [7] in $H_2SO_4$. In aqueous solution the substitution of deuterium for hydrogen generally decreases the dissociation constant of an acid by a factor of three to four.[8]

TABLE 7. *Calculation of the basic dissociation constant of deuterium oxide.*

| Concn. (m) | F. p. (obs.) | F. p. (corr.) | $\theta$ | $g\nu$ | $g$ | $\nu$ | $K_b$ | |
|---|---|---|---|---|---|---|---|---|
| 0·00 | 14·347° | 14·502° | — | — | — | — | — | |
| 0·02 | 14·237 | 14·260 | 0·242° | 1·87 | 0·981 | 1·91 | 0·20 | Mean 0·23 |
| 0·04 | 14·030 | 14·036 | 0·466 | 1·80 | 0·984 | 1·83 | 0·16 | |
| 0·06 | 13·803 | 13·806 | 0·696 | 1·79 | 0·980 | 1·81 | 0·21 | |
| 0·08 | 13·578 | 13·580 | 0·922 | 1·78 | 0·996 | 1·79 | 0·24 | |
| 0·10 | 13·353 | 13·354 | 1·148 | 1·77 | 1·002 | 1·76 | 0·24 | |
| 0·12 | 13·135 | 13·135 | 1·367 | 1·76 | 1·008 | 1·75 | 0·27 | |
| 0·14 | 12·920 | 12·920 | 1·582 | 1·75 | 1·014 | 1·72 | 0·26 | |

*An Improved Estimate of the Extent of Self-dissociation of Dideuterosulphuric Acid.*—It was assumed earlier in the calculation of the extent of the self-dissociation of dideuterosulphuric acid that the dideuterodisulphuric acid ($D_2S_2O_7$) produced by the self-dissociation is not ionised. This is only a rough approximation and, by using the value of the dissociation constant of dideuterodisulphuric acid calculated above, the calculation of the concentrations of the self-dissociation products of dideuterosulphuric acid can be somewhat improved. The concentration of dideuterodisulphuric acid produced by the self-dissociation being 0·008m, from the acid dissociation of dideuterodisulphuric acid ($K_a = 2 \times 10^{-3}$) the degree of dissociation of a solution of dideuterodisulphuric acid having this stoicheiometric concentration is readily shown to be 40%. It is reasonable to assume that the dideuterodisulphuric acid produced in the self-dissociation reaction is ionised approximately to the same extent. If allowance is made in eqn. (4) for the ionisation of dideuterodisulphuric acid by putting $a = 1·4$ and $n = 3·4$ it is found that the total concentration of self-dissociation products is 0·033m and that the individual concentrations of self-dissociation products are as given in Table 9. From these concentrations values of the autodeuterolysis constant $K_{ad}$ and the ionic self-dehydration constant $K_{id}$ can be calculated; $K_{ad} = [D_3SO_4^+][DSO_4^-] = K_{id} = [D_3O^+][DS_2O_7^-] = 4 \times 10^{-5}$ mole$^2$ l.$^{-2}$.

TABLE 8. *Calculation of the acid dissociation constant of dideuterodisulphuric acid.*

| Concn. (m) | F. p. | $\theta$ | $\nu$ | $10^3K_a$ | |
|---|---|---|---|---|---|
| 0·00 | (14·502°) | — | — | — | |
| 0·08 | 13·910 | 0·592° | 1·15 | 2·1 | Mean 2·4 |
| 0·12 | 13·645 | 0·857 | 1·12 | 1·9 | |
| 0·16 | 13·370 | 1·132 | 1·10 | 2·2 | |
| 0·20 | 13·100 | 1·402 | 1·10 | 2·2 | |
| 0·24 | 12·824 | 1·678 | 1·10 | 2·7 | |
| 0·28 | 12·550 | 1·952 | 1·10 | 3·1 | |

TABLE 9. *Approximate concentrations of the self-dissociation products of dideuterosulphuric acid.*

| | Molality |
|---|---|
| $DSO_4^-$ | 0·010 |
| $D_3SO_4^+$ | 0·004 |
| $DS_2O_7^-$ | 0·004 |
| $D_3O^+$ | 0·010 |
| $D_2S_2O_7$ | 0·006 |
| Total | 0·034 |

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

[8] See, for example, Gurney, "Ionic Processes in Solution," McGraw-Hill, London, 1953.

*The Ionisation of* m-*Nitrotoluene.*—The ionisation of weak bases in sulphuric acid has been studied previously [9, 10, 11, 12] and it was therefore of interest to compare the extent of ionisation of a weak base in dideuterosulphuric acid with its degree of ionisation in sulphuric acid. *m*-Nitrotoluene was chosen, and the results of the measurements of the conductivity of its solutions in dideuterosulphuric acid are given in Table 10. The conductivity of its solutions changed very slowly with time although over the period of 2 hr. during which the measurements recorded in Table 10 were made this drift in the conductivity was quite negligible: it could be caused by the deuteration of the *m*-nitrotoluene which would be expected to be very slow under the experimental conditions. By comparing the conductivities with those of $KDSO_4$ solutions (Table 2) the degree of ionisation of *m*-nitrotoluene at various concentrations could be calculated by the method of Gillespie and Solomons [11] and hence values of $K_b = [R{\cdot}NO_2D^+][DSO_4^-]/[R{\cdot}NO_2]$ were obtained. The mean value was $K_b$ ($D_2SO_4$) = 0·012 mole kg.$^{-1}$ which can be compared with the value $K_b$ ($H_2SO_4$) = 0·023 mole kg.$^{-1}$ given by Gillespie and Solomons.[11] Thus *m*-nitroluene is less ionised in $D_2SO_4$ than in $H_2SO_4$ and this can probably be attributed to $H_2SO_4$ being a slightly stronger acid than $D_2SO_4$. The alternative explanation that $CH_3{\cdot}C_6H_4{\cdot}NO_2D^+$ is a stronger acid than $CH_3{\cdot}C_6H_4{\cdot}NO_2H^+$ seems less probable since it is generally found that substitution of hydrogen by deuterium reduces the strength of an acid.

TABLE 10. *Specific conductances of solutions of* m-*nitrotoluene at* 25°.

| Concn. (mole $kg._{soln.}^{-1}$) | 0·0000 | 0·0109 | 0·1205 | 0·1952 | 0·2698 | 0·3690 |
|---|---|---|---|---|---|---|
| $\kappa$ ($10^{-2}$ ohm$^{-1}$ cm.$^{-1}$) | 0·257 | 0·272 | 0·402 | 0·574 | 0·638 | 0·695 |

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[9] Gillespie, *J.*, 1950, 2542.

[10] Brand, Horning, and Thornley, *J.*, 1952, 1374.

[11] Gillespie and Solomons, *J.*, 1957, 1796.

[12] Gillespie and Robinson, *J.*, 1957, 4233.