17. *Solutions in Sulphuric Acid. Part XVII.* Cryoscopic Measurements on Some Univalent Metal Sulphates.*

By R. J. Gillespie and J. V. Oubridge.

Earlier cryoscopic measurements on solutions of potassium and ammonium sulphates in sulphuric acid (Part I, Gillespie, Hughes, and Ingold, *J.*, 1950, 2473) have been repeated and new measurements have been made on lithium, sodium, cæsium, silver, and thallous sulphates. It has been shown that osmotic coefficients calculated from the experimental results for all the electrolytes studied may be fitted to an extended form of the Debye–Hückel equation using a value of the dielectric constant of 115 at 10° c. Some information concerning the solvation of the lithium, sodium, potassium, cæsium, and ammonium ions has also been obtained, and the possibility of incomplete dissociation of silver and thallous hydrogen sulphates is discussed.

BECAUSE of the apparently close agreement between the experimental freezing-point depressions obtained for a wide variety of solutes, both organic and inorganic, and the corresponding ideal freezing-point depressions if allowance was made in most cases for some solvation of the formed ions, it was suggested in Part I (*loc. cit.*) that the measurements supported the earlier conclusion by Treffers and Hammett (*J. Amer. Chem. Soc.*, 1937, **59**, 1788) that interionic forces in sulphuric acid are negligibly small. It was further suggested that this could be plausibly accounted for if sulphuric acid had a very high dielectric constant. There are now, however, several reasons why this earlier work needs re-examination and some re-interpretation. First, most of the measurements on which these conclusions were based were made in slightly aqueous sulphuric acid and, as was first pointed out in Part VIII (Gillespie, *J.*, 1950, 2997), the exact interpretation of the results is complicated because of the need to take into account any incompleteness in the repression

* Part XVI, *J.*, 1954, 1851.

of the self-ionisation of the solvent, the possibility that the ionisation of the water is repressed by the added solute, and the solvation of the ions formed by the ionisation of the water. Secondly, a more accurate value for the cryoscopic constant of 6·12 may be calculated (Part XVI, Gillespie, *J.*, 1954, 1851) from Rubin and Giauque's determination of the heat of fusion of sulphuric acid (*J. Amer. Chem. Soc.*, 1952, **74**, 800). Thirdly, Brand, James, and Rutherford (*J.*, 1953, 2447) have given a value of 110 at 25° c for the static dielectric constant of sulphuric acid extrapolated from dielectric absorption measurements in the frequency range 300—3000 Mc, and this value has been approximately confirmed by Gillespie and White (unpublished measurements) using Furth's " ellipsoid method " (*Z. Physik*, 1924, **22**, 98).

Previous cryoscopic measurements on ammonium and potassium sulphates in 100% sulphuric acid (Part I, *loc. cit.*) have now been repeated and extended to a number of other metal sulphates in order to provide a sufficient body of results, the interpretation of which would be free from the ambiguities resulting from the presence of water, and which could be used to determine how far the earlier conclusions concerning the behaviour of electrolytes in sulphuric acid could still be regarded as valid.

EXPERIMENTAL

The apparatus and general procedure for making the cryoscopic measurements have been described previously (Part I, *loc. cit.*). Freezing points were measured either with a platinum resistance thermometer and a Smith's difference bridge as described in Part I, or with a solid-stem mercury-in-glass thermometer (Part XIV, Gillespie and Leisten, *J.*, 1954, 1) which was periodically calibrated against the platinum resistance thermometer.

The solvent used in all cases was sulphuric acid of maximum freezing point, which was prepared as follows : A dilute oleum was first prepared from " AnalaR " 98% sulphuric acid and sulphur trioxide distilled from 65% oleum. Approximately 1 l. of this acid was then partially frozen in a 2-l. three-necked flask, and the freezing point observed while aqueous acid was added with good stirring until the maximum freezing point had been reached. Each sample of sulphuric acid used in an experiment was then finally adjusted to exactly the maximum freezing point in the freezing-point cell by the addition of small weighed quantities of aqueous acid or oleum, immediately before beginning the experiment.

All the metal sulphates were of " AnalaR " purity and were dried in an oven at 120° and stored in desiccators over phosphoric oxide.

A supercooling correction of $\delta T = 0.0125s\theta$, where s is the amount of supercooling and θ the observed freezing-point depression, was applied to all the observed freezing points (Part I, *loc. cit.*). The numerical factor 0·0125, which differs slightly from the value of 0·012 used in the earlier Parts of this series, is based on the value of the heat of fusion of 2560 cal. (Rubin and Giauque, *loc. cit.*).

RESULTS

Because of the large number of freezing points measured the results are not presented in detail but are given in the form of a Table giving the freezing points of the solutions at certain definite concentrations in order to facilitate the comparison of the different electrolytes investigated. These freezing points were obtained from large-scale plots of the experimental results. A smooth curve was drawn through the experimental points for at least three and

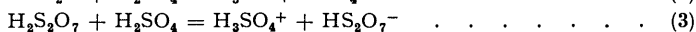TABLE 1. *Freezing points of solutions of univalent metal sulphates.*

Molality	Na_2SO_4	K_2SO_4	Li_2SO_4	Cs_2SO_4	$(NH_4)_2SO_4$	Tl_2SO_4	Ag_2SO_4
0·00	10·365°	10·365°	10·365°	10·365°	10·365°	10·365°	10·365°
0·01	10·200	10·203	10·203	10·205	10·205	10·208	10·208
0·02	9·985	9·990	9·990	9·995	9·996	10·000	10·002
0·03	9·745	9·757	9·754	9·764	9·770	9·782	9·780
0·04	9·501	9·518	9·518	9·526	9·540	9·553	9·555
0·05	9·251	9·276	9·280	9·286	9·305	9·328	9·326
0·06	8·994	9·027	9·030	9·043	9·068	9·100	9·097
0·07	8·736	8·772	8·780	8·800	8·827	8·867	8·868
0·08	8·472	8·516	8·525	8·558	8·588	8·637	8·638
0·09	8·208	8·261	8·272	8·311	8·348	8·404	8·414
0·10	7·940	8·007	8·026	8·060	8·105	8·170	8·185
0·11	7·670	7·751	7·762	7·805	7·860	—	7·953
0·12	7·397	7·492	7·498	—	7·615	—	—

generally more experiments for each electrolyte in each of which from five to twelve additions of the solute were made. The freezing points obtained in this way for solutions of sodium, potassium, lithium, cæsium, ammonium, thallous, and silver sulphates are given in Table 1.

DISCUSSION

The Freezing Point of Sulphuric Acid.—In Part I (*loc. cit.*) the freezing point of sulphuric acid was given as 10·36° ± 0·01°. Shortly after the publication of that work Gable, Betz, and Maron (*J. Amer. Chem. Soc.*, 1950, **72**, 1445) obtained the value of 10·37°, and this was later confirmed by Kunzler and Giauque (*ibid.*, 1952, **74**, 297) who gave a value of 10·371°. The highest value of the freezing point that we have been able to obtain consistently is 10·365° and the small difference between this value and 10·371° may be attributed to inaccuracies in the calibration of our thermometers and perhaps to slight impurities in our acid. For the purpose of the present discussion, in which we are concerned only with freezing-point depressions, we have adopted 10·365° as the freezing point of sulphuric acid. Occasionally sulphuric acid was used which had a freezing point that was a few thousandths of a degree lower and in such cases all the observed freezing points of solutions in these samples of acid were corrected by adding the difference between the initial freezing-point of the acid and 10·365°. The procedure is justifiable if the impurity in the sulphuric acid causing the freezing-point lowering is neither sulphur trioxide nor water and if it does not react in any way with the added solute. It is probable that any impurity that was present was, in fact, not sulphur trioxide or water since the freezing point was carefully adjusted to as near as possible the maximum value by addition of oleum or aqueous acid. In any case the values of the freezing points given in Table 1 are based only on the experiments in which the initial freezing point of the acid did not differ by more than a few thousandths of a degree from 10·365° and in which duplicate runs after correction to correspond to a maximum freezing point of 10·365° gave agreement to within 0·02° at the highest concentrations.

The Self-dissociation Equilibria in Sulphuric Acid.—The calculation and interpretation of the osmotic coefficients of solutions of electrolytes in sulphuric acid is considerably affected by the fact that sulphuric acid undergoes appreciable self-dissociation, and it is therefore necessary to consider this self-dissociation in some detail. In Part I (*loc. cit.*), Part II (Gillespie, *J.*, 1950, 2493), and Part IV (*idem, J.*, 1950, 2516) it was shown that the self-dissociation occurs according to the equations :

$$2H_2SO_4 = H_2O + H_2S_2O_7 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$
$$H_2O + H_2SO_4 = H_3O^+ + HSO_4^- \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$
$$H_2S_2O_7 + H_2SO_4 = H_3SO_4^+ + HS_2O_7^- \quad . \quad . \quad . \quad . \quad . \quad (3)$$
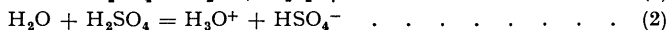
and that there will also be set up the equilibria :

$$2H_2SO_4 = H_3SO_4^+ + HSO_4^- \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

and

$$2H_2SO_4 = H_3O^+ + HS_2O_7^- \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Reaction (4) is simply the autoprotolysis of the solvent, and reaction (5) was termed the ionic self-dehydration. It was assumed as a first approximation that reactions (2) and (3) go essentially to completion and it was shown that the concentrations of the self-dissociation ions are determined by two equilibrium constants

$$K_{ap} = [H_3SO_4^+][HSO_4^-] = 1·7 \times 10^{-4} \text{ mole}^2 \text{ kg.}^{-2}$$
$$K_{id} = [H_3O^+][HS_2O_7^-] = 0·7 \times 10^{-4} \text{ mole}^2 \text{ kg.}^{-4}$$

The value of the autoprotolysis constant is of particular importance to our present discussion and we have recalculated it using the new value of the cryoscopic constant and the observed freezing-point curves of all the electrolytes investigated except silver and thallous sulphates.

The addition to sulphuric acid of any solute that produces hydrogen sulphate ions will

modify the concentrations of the self-dissociation products, and in so far as the approxim-
ation made above is correct it will repress the autoprotolysis leaving the concentration of
hydroxonium and hydrogen disulphate ions unchanged. The observed freezing points for
solutions of such an electrolyte may be used to obtain a value for the autoprotolysis
constant. By assuming a reasonable approximate value for this quantity, the observed
freezing-point curve may be corrected to obtain an approximation to the freezing-point
curve that would be given by the solute in a hypothetical acid with zero concentration of
autoprotolytic ions, and extrapolation of this curve to zero concentration of added solute
gives the freezing point (T_0') of this hypothetical acid. From the difference between this
freezing point and the observed freezing point of sulphuric acid, the concentration of the
autoprotolytic ions and hence an improved value of the autoprotolysis constant K_{ap} may be
calculated. The calculations may be repeated until self-consistent values of the freezing
point of the hypothetical acid and the autoprotolysis constant are obtained and until the
corrected freezing-point curve agrees, apart from small deviations due to non-ideality, with
the ideal calculated freezing-point curve referred to the freezing point (T_0') of the
hypothetical acid. The value thus obtained was $T_0' = 10.515° \pm 0.01°$, which differs
only slightly from the value $10.52° \pm 0.02°$ given in Part I. The molality of the auto-
protolysis ions is then given by $m_{ap} = \theta/gk_f = 0.0250$, where $\theta = 10.515 - 10.365 =$
0.150 and the osmotic coefficient $g = 0.981$ (see p. 87). Hence $[H_3SO_4^+] = [HSO_4^-] =$
$0.0125m$, and $K_{ap} = [H_3SO_4^+][HSO_4^-] = 1.56 \times 10^{-4}$.

All the self-dissociation equilibria are of course repressed by the addition of either water
or sulphur trioxide, and the hypothetical freezing point (T_0'') of completely undissociated
sulphuric acid may be obtained from the freezing-point depressions produced by sulphur
trioxide and water by extrapolation in a similar manner to that outlined above. It has
been shown in Part II that $T_0'' - T_0' = 0.100°$ and hence we shall now assign the freezing
point of the hypothetical undissociated acid the value of $10.615°$, which differs only slightly
from the value of 10.62 given in Part II. If the freezing-point depression $T_0'' - T_0' =$
$0.100°$ is assumed to be entirely due to the ions H_3O^+ and $HS_2O_7^-$ it corresponds to a value
of K_{id} of 7×10^{-5}.

These values of K_{id} and K_{ap} are only approximately correct; the assumptions on which
they are based are known not to be exact as it was shown in Part II that water and
disulphuric acid are incompletely ionised. It was believed that the errors introduced by
the assumptions that water and disulphuric acid are completely ionised were, however,
insignificant, and this has now been verified by Gillespie and Solomons (unpublished work)
who have calculated the concentrations of all the self-dissociation products in the presence
of an electrolyte $MHSO_4$, taking into account the incomplete ionisation of water and
disulphuric acid, and have obtained more accurate values of K_{ap} and K_{id}, which are slightly
smaller than those given above. Their work shows that the concentrations of un-ionised
water and disulphuric acid are in fact not negligible but that, nevertheless, the extrapolation
procedure described above to obtain T_0'' is of sufficient accuracy for our present purpose,
and that, also, the freezing-point depression produced by the products of the self-
dissociation for any concentration of added electrolyte $MHSO_4$, in the range with which we
are concerned, may be calculated with sufficient accuracy (*i.e.*, to within $0.002°$) by the
procedure used previously, based on the approximate values of K_{ap} and K_{id}, ignoring the
small concentrations of un-ionised water and disulphuric acid. We shall therefore
continue to use this method in the present paper.

The Calculation of Osmotic Coefficients.—The equation relating the freezing-point
depression θ to the molality m_2 of the solute may be obtained by a slight modification of
equation 7 of Part XVI and is

$$\theta/m_2 = gv_2k_f\left\{1 - \left(\frac{1}{T_0} - \frac{\Delta C_p}{2\Delta H_0'}\right)\theta\right\}\left\{1 + \frac{(2s_2 - v_2)m_2}{2m_1}\right\} \quad . \quad . \quad . \quad (1)$$

where v_2 is the number of moles of ions formed from one mole of the solute, k_f is
the cryoscopic constant, T_0 is the freezing point of the pure solvent, ΔC_p is the difference
between the heat capacities of the solid and liquid solvent, m_1 is the molality of the solvent,

s_2 is the total number of moles of the solvent required to react with and solvate the ions formed by one mole of the solute, and g is the rational osmotic coefficient of the solvent.

The factor $(1/T_0) - (\Delta C_p/2\Delta H_0{}^f)$ may be computed to be 0·00195 deg.$^{-1}$ from the following values : $\Delta H_0{}^f = 2560$ cal. mole^{-1} (Rubin and Giauque, *loc. cit.*), $T_0 = 10·37° = 283·5°$ K (Kunzler and Giauque, *loc. cit.*), and $\Delta C_p = 8·7$ cal. mole^{-1} deg.$^{-1}$ (Rubin and Giauque, *loc. cit.*). The value of k_f has been given as 6·12 in Part XVI (*loc. cit.*). Hence we may write for any solute

$$\theta/m_2 = 6·12\nu_2 g'(1 - 0·00195\theta)\left\{1 + \frac{(2s_2 - \nu_2)}{2m_1} m_2\right\} \quad . \quad . \quad . \quad (2)$$

where we now denote the osmotic coefficient by g' to indicate that it is calculated on the basis of solvated ions. We shall henceforth use the unprimed symbol g for the osmotic coefficient calculated on the assumption that the ions are not solvated.

It is convenient for our present discussion to divide s_2 into two parts, namely, the number of moles of solvent s_2' that react with one mole of the added solute and the number of moles of solvent s_2'' that are required to solvate the ions and molecules formed in solution from one mole of solute. Thus we have $s_2 = s_2' + s_2''$. For an electrolyte M_2SO_4 ionising according to the equation

$$M_2SO_4 + H_2SO_4 \rightleftharpoons 2M^+ + 2HSO_4^- \quad . \quad . \quad . \quad . \quad . \quad (A)$$
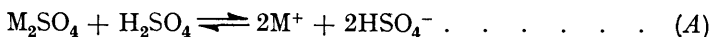
we have that $\nu_2 = 4$ and $s_2' = 1$. Hence equation 2 may be written in the form

$$\theta/m_2 = 24·48g'(1 - 0·00195\theta)(1 - m_2/m_1 + s_2''m_2/m_1) \quad . \quad . \quad . \quad (3)$$

We may, if we wish, make ionic solvation part of the general non-ideality and set $s_2'' = 0$; we then have

$$\theta/m_2 = 24·48g(1 - 0·00195\theta)(1 - m_2/m_1) \quad . \quad . \quad . \quad . \quad (4)$$

and for an ideal electrolyte

$$\theta/m_2 = 24·48(1 - 0·00195\theta)(1 - m_2/m_1) \quad . \quad . \quad . \quad . \quad (5)$$

From equations (4) and (5) we have that

$$g = \theta_{observed}/\theta_{ideal} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

The hypothetical completely undissociated acid has been chosen as the standard state in calculating osmotic coefficients. Thus the observed freezing-point depressions have been calculated from the freezing-point (T_0'') of the hypothetical undissociated acid, *viz.*, 10·615°, using the observed freezing points listed in Table 1. These freezing-point depressions are given in Table 2. The freezing-point depression for an ideal electrolyte M_2SO_4 at any concentration is the sum of the depression that it would produce in the completely undissociated solvent and the depression caused by the ions resulting from the self-dissociation at that concentration of added electrolyte. Table 3 shows the calculation of the freezing-point depressions of an ideal electrolyte M_2SO_4. These values were used together with the observed values for the different electrolytes given in Table 2 to calculate

TABLE 2. *Freezing-point depressions produced by univalent metal sulphates.*

Molality	Na_2SO_4	K_2SO_4	Li_2SO_4	Cs_2SO_4	$(NH_4)_2SO_4$	Tl_2SO_4	Ag_2SO_4
0·01	0·415°	0·412°	0·412°	0·410°	0·410°	0·407°	0·407°
0·02	0·630	0·625	0·626	0·620	0·619	0·615	0·613
0·03	0·870	0·858	0·861	0·851	0·845	0·833	0·835
0·04	1·114	1·097	1·097	1·089	1·075	1·062	1·060
0·05	1·364	1·339	1·335	1·329	1·310	1·287	1·289
0·06	1·621	1·588	1·585	1·572	1·547	1·515	1·518
0·07	1·879	1·843	1·835	1·815	1·788	1·748	1·747
0·08	2·143	2·099	2·090	2·057	2·027	1·978	1·977
0·09	2·407	2·354	2·345	2·304	2·267	2·211	2·201
0·10	2·675	2·608	2·595	2·555	2·510	2·445	2·430
0·11	2·945	2·864	2·853	2·810	2·755	—	2·662
0·12	3·218	3·123	3·117	—	3·000	—	—

TABLE 3. *Freezing-point depressions produced by an ideal electrolyte* M_2SO_4.

Molality	θ * (°C)	δ_1 † (°C)	δ_2 ‡ (°C)	θ_{ideal} $(\theta + \delta_1 + \delta_2)$ (°C)	Molality	θ * (°C)	δ_1 † (°C)	δ_2 ‡ (°C)	θ_{ideal} $(\theta + \delta_1 + \delta_2)$ (°C)
0·01	0·244	0·075	0·100	0·419	0·08	1·937	0·012	0·100	2·049
0·02	0·488	0·044	,,	0·632	0·09	2·176	0·011	,,	2·287
0·03	0·732	0·032	,,	0·864	0·10	2·415	0·010	,,	2·525
0·04	0·974	0·024	,,	1·098	0·11	2·653	0·009	,,	2·762
0·05	1·216	0·019	,,	1·335	0·12	2·890	0·008	,,	2·998
0·06	1·457	0·016	,,	1·573	0·13	3·126	0·007	,,	3·233
0·07	1·697	0·014	,,	1·811	0·14	3·362	0·007	,,	3·469

* Calc. by means of eqn. (5) for an ideal electrolyte in the hypothetical undissociated solvent.
† Freezing-point depression caused by the ions remaining from the autoprotolysis calculated from $K_{ap} = 1.56 \times 10^{-4}$ and eqn. (5).
‡ Freezing-point depression caused by the constant concentration of ions resulting from the ionic self-dehydration.

TABLE 4. *Osmotic coefficients of solutions of univalent metal sulphates.*

Molality	Na_2SO_4	K_2SO_4	Li_2SO_4	Cs_2SO_4	$(NH_4)_2SO_4$	Tl_2SO_4	Ag_2SO_4
0·01	0·990	0·983	0·983	0·979	0·979	0·971	0·972
0·02	0·997	0·989	0·989	0·981	9·080	0·973	0·970
0·03	1·007	0·993	0·996	0·985	0·978	0·964	0·969
0·04	1·014	0·999	0·999	0·992	0·979	0·967	0·967
0·05	1·023	1·001	1·000	0·995	0·981	0·964	0·965
0·06	1·031	1·010	1·008	0·999	0·983	0·963	0·965
0·07	1·038	1·017	1·014	1·002	0·987	0·965	0·964
0·08	1·046	1·024	1·020	1·004	0·990	0·966	0·965
0·09	1·054	1·029	1·024	1·007	0·991	0·967	0·962
0·10	1·059	1·034	1·028	1·012	0·994	0·968	0·962
0·11	1·066	1·037	1·033	1·018	0·997	—	0·964
0·12	1·073	1·042	1·040	—	1·000	—	—

osmotic coefficients by means of equation (6). The osmotic coefficients thus obtained are listed in Table 4. These osmotic coefficients are therefore values for solutions of the various electrolytes containing also small concentrations of residual self-dissociation ions. The concentrations of the self-dissociation ions are relatively small except at the lowest concentrations of added electrolyte. Thus the depression produced by the self-dissociation ions amounts to 12% of the total depression in a 0·03-molal solution of M_2SO_4, and 4% in a 0·1-molal solution.

The self-dissociation of sulphuric acid gives rise to another slight complication in the interpretation of the osmotic coefficients. The experimental value of the heat of fusion from which the cryoscopic constant has been calculated includes the heat of self-dissociation, and therefore this value of the cryoscopic constant will not be exactly equal to the true value which relates to the hypothetical undissociated acid as the standard state (Wyatt, *J.*, 1953, 1175). Hence osmotic coefficients calculated on the basis of our cryoscopic constant will include a factor equal to the ratio of the true cryoscopic constant to our value. Fortunately it was shown in Part XVI that the contribution of the heat of autoprotolysis to the heat of fusion is probably only approximately 4 cal., which is of the same order of magnitude as the experimental error in the heat of fusion (± 3 cal.), and is too small to be detected in our experiments.

Comparison with the Debye–Hückel Theory.—The rational osmotic coefficient g of the solvent is given, according to the Debye–Hückel theory, by the equation

$$g = 1 - \frac{2.303}{3} A|z_1 z_2|I^{\frac{1}{2}} \sigma(x) \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where $x = B\mathring{a}I^{\frac{1}{2}}$ ($\mathring{a}$ is the distance of closest approach of the anion and cation in Ångström units).

$$\sigma(x) = \frac{3}{x^3}\left[(1 + x) - 2\ln(1 + x) - \frac{1}{1 + x}\right],$$

$$A = \left(\frac{2\pi N}{1000}\right)^{\frac{1}{2}} \frac{e^3}{2.303(\epsilon kT)^{\frac{3}{2}}} \qquad 10^8 B = \left(\frac{8\pi Ne^2}{1000\epsilon kT}\right)^{\frac{1}{2}}$$

I is the ionic strength $= \frac{1}{2}\Sigma cz_i^2$ (c_i is the molar concentration of the ion i and z_i its valency), z_1 and z_2 are the valencies of the cations and anions respectively, and ε is the dielectric constant of the solvent (see, *e.g.*, Robinson and Stokes, " Electrolyte Solutions," Butterworths, London, 1954, p. 233).

Now we have approximately that $c = m\rho_0$, where ρ_0 is the density of the pure solvent and for an electrolyte M_2SO_4 [cf. eqn. (A)], $z_1 = z_2 = 1$ and $I = 2m\rho_0$.

Hence :

$$g = 1 - A'(2m)^{\frac{1}{2}}\sigma(x') \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

where

$$x' = B'\mathring{a}(2m)^{\frac{1}{2}}$$

$$A' = \left(\frac{2\pi\rho N_0}{9000}\right)^{\frac{1}{2}}\left(\frac{e^2}{\varepsilon kT}\right)^{\frac{3}{2}} = 0.321$$

and

$$B' = \left(\frac{8\pi Ne^2}{1000\varepsilon kT}\right)^{\frac{1}{2}} = 0.376$$

taking $\rho_0 = 1.827$ (Part XI, Gillespie and Wasif, *J.*, 1953, 215) and $\varepsilon = 115$. Therefore

$$g = 1 - 0.321(2m)^{\frac{1}{2}}\sigma\{0.376\mathring{a}(2m)^{\frac{1}{2}}\} \quad . \quad . \quad . \quad . \quad . \quad (9)$$

If we set $\mathring{a} = 0$ we obtain the Debye–Hückel limiting law for an electrolyte M_2SO_4 in sulphuric acid :

$$g = 1 - 0.321(2m)^{\frac{1}{2}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

The value of the dielectric constant of sulphuric acid at 10° c is unfortunately rather uncertain. Brand, James, and Rutherford (*loc. cit.*) obtained the value of 110 at 20° and suggested the value of 115 at 10°. Gillespie and White (*loc. cit.*) obtained limiting values of 98 and 121 at ~20°, and of 108 and 135 at ~10°. The choice of 115 at 10° therefore seems reasonable, at least as a preliminary value.

We shall find it convenient to express concentrations in terms of the molal ionic strength $\mu = \frac{1}{2}\Sigma m_i z_i^2$, and equations (9) and (10) may then be written :

$$g = 1 - 0.321\,\mu^{\frac{1}{2}}\sigma(0.376\mathring{a}\mu^{\frac{1}{2}}) \quad . \quad . \quad . \quad . \quad . \quad (11)$$

and

$$g = 1 - 0.321\mu^{\frac{1}{2}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

In the Figure, the osmotic coefficients for the electrolytes lithium, sodium, potassium, cæsium, ammonium, thallous, and silver sulphates, have been plotted against $\mu^{\frac{1}{2}}$, where $\mu = 2m + m_{ap} + m_{id}$. It may be noted that it is not possible to obtain a solution in sulphuric acid having $\mu < m_{ap} + m_{id} = 0.0125 + 0.0083 = 0.0208$ or $\mu^{\frac{1}{2}} < 0.1442$. This ionic strength is indicated by the vertical line in the Figure. It may also be noted that the curves for all the electrolytes in the figure must extrapolate to the value $g = 0.981$ at $\mu^{\frac{1}{2}} = 0.1442$, since this is the value chosen for the osmotic coefficient of pure sulphuric acid, *i.e.*, sulphuric acid containing the products of its self-dissociation (see p. 87).

It is found that the osmotic coefficients for sodium, potassium, lithium, cæsium, and ammonium sulphates are greater than predicted by equation (11) for any reasonable value of $\mathring{a}$, and they increase more rapidly with increasing concentration at high concentrations than is consistent with an equation of this form. This type of behaviour is generally attributed, particularly in aqueous solutions, to short-range forces, especially between the ions and the solvent, becoming of comparable importance to the long-range interionic forces that are considered by the Debye–Hückel theory. It has been common practice to allow for the effect of these short-range forces by adding an empirical linear term to the Debye–Hückel expression. If we do this for sulphuric acid we may write :

$$g = 1 - 0.321\mu^{\frac{1}{2}}\sigma(0.376\mathring{a}\mu^{\frac{1}{2}}) + b\mu \quad . \quad . \quad . \quad . \quad . \quad (13)$$

where b is an empirical constant. It may be seen from the Figure that this equation will fit the observed osmotic coefficients of sodium, lithium, potassium, cæsium, and ammonium

sulphates with $\mathring{d} = 10$ and with values of $b = 0.45$, 0.3, 0.3, 0.2, and 0.1 respectively. These values have been chosen so as to give reasonably good agreement between the calculated curves and the experimental results, but they are not necessarily the best possible values that could have been chosen, as it was not considered that the accuracy of the present results was sufficient to warrant an attempt to obtain such values. Only very approximate agreement between these calculated curves and the experimental results is to be expected at the lowest concentrations investigated, partly because the experimental

Comparison of experimental osmotic coefficients with those predicted by equation (13).

$\mu^{1/2}$ (μ = molal ionic strength)
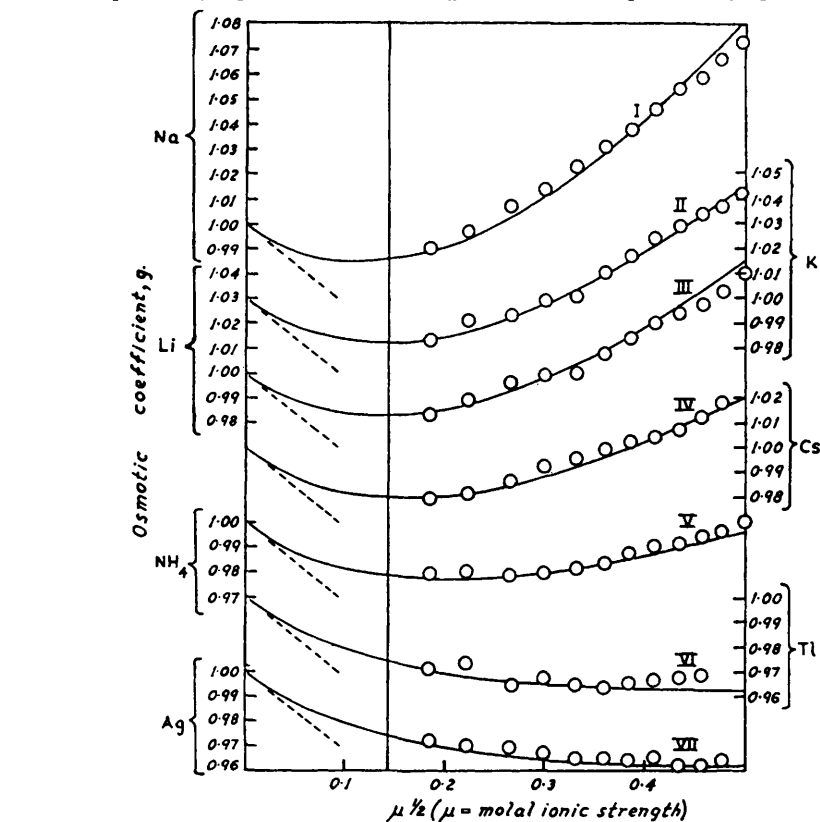
   ◯   Experimental values.
– – – –   Limiting Debye–Hückel slope (eqn. 12).
————   Calc. from eqn. (13) with the values of the parameters $\mathring{d}$ and b given below.

		$\mathring{d}$	b			$\mathring{d}$	b
I	NaHSO$_4$	10	0.45	V	NH$_4$·HSO$_4$	10	0.1
II	KHSO$_4$	10	0.3	VI	TlHSO$_4$	8	0
III	LiHSO$_4$	10	0.3	VII	AgHSO$_4$	8	0
IV	CsHSO$_4$	10	0.2				

error of the measurement of the freezing-point depression increases at low concentrations, and partly because the curves are calculated for a single electrolyte, whereas at low concentrations the self-dissociation products make an appreciable contribution to the total ionic strength. As pointed out earlier, the observed osmotic coefficients for all the electrolytes must extrapolate to the value 0.981 at $\mu^{1/2} = 0.1442$, which is the value that was assigned to the osmotic coefficient of pure sulphuric acid. This value was chosen as the mean of the osmotic coefficients at $\mu^{1/2} = 0.1442$ of 0.978 and 0.984, calculated for the values $\mathring{d} = 10$ and $b = 0.1$ and 0.4 respectively.

The agreement between the calculated curves and the experimental results enables us

to conclude that they are not inconsistent with the value of 115 for the static dielectric constant of sulphuric acid, and therefore they lend a certain support to this value. The same conclusion has been reached by Brand, James, and Rutherford (*loc. cit.*), who showed that our earlier results on the freezing points of solutions of potassium and ammonium sulphates and nitric acid in sulphuric acid containing a little water could be fitted approximately by a simplified form of equation (13) due to Guggenheim (*Phil. Mag.*, 1935, **19**, 588) in which $\mathring{a}B'$ is arbitrarily set equal to unity. It must be realised, however, that a change of as much as 10% in the above value of the dielectric constant would produce an effect on the calculated curves that would only be just sufficient to make them inconsistent with our experimental results. There is certainly no reason, however, for thinking as we did formerly (Part I, *loc. cit.*) that sulphuric acid has a very high " ferroelectric " dielectric constant. This conclusion was based on our earlier observations (Part I, *loc. cit.*) and those of Treffers and Hammett (*loc. cit.*) that solutions of electrolytes in sulphuric acid apparently behave almost ideally, especially if some allowance is made for ion solvation. The apparent ideality may be attributed to the fact that the lowest ionic concentration obtainable in sulphuric acid is 0·02 molal and at this concentration, as may be seen from the Figure, the effects of ion–solvent interactions are becoming more important than those due to interionic forces. Thus, if as was implicitly assumed, the osmotic coefficient for sulphuric acid in the pure acid is taken as unity, then at no concentration of an added electrolyte such as potassium sulphate would the osmotic coefficient be less than unity and hence no deviations from ideality that could be attributed directly to interionic forces would be observed. In the single case in which, at the time, freezing-point depressions had been obtained which were less than ideal, namely, for the electrolyte water, it was reasonably assumed that ionisation was incomplete.

Ionic Solvation.—Following our earlier work (Parts I and II, *loc. cit.*) and the very successful treatment by Stokes and Robinson (*J. Amer. Chem. Soc.*, 1948, **70**, 1870) of ionic activity coefficients in aqueous solution in terms of ion–solvent interactions we may suppose that the most important contribution to the linear term in equation (13) comes from ion–solvent interactions, or in other words ion solvation. Now equation (3) may be written (with sufficient accuracy) in the form

$$\theta/m_2 = 24\cdot48g'(1 - 0\cdot001956\theta)(1 - m_2/m_1)(1 + s_2''m_2/m_1) \quad . \quad . \quad . \quad (14)$$

from which by comparison with equation (4) it may be seen that

$$g = g'(1 + s_2''m_2/m_1) \quad . \quad . \quad . \quad . \quad . \quad (15)$$

Now if we assume that the Debye–Hückel expression (9) gives the osmotic coefficient referred to solvated ions, *i.e.*, that it gives g' and not g (Stokes and Robinson, *loc. cit.*), then we may write for the osmotic coefficient g

$$g = \{1 - 0\cdot321\mu^{\frac{1}{2}}\sigma(0\cdot376\mathring{a}\mu^{\frac{1}{2}})\}(1 + s_2''m_2/m_1) \quad . \quad . \quad . \quad (16)$$

or, more simply, and to a sufficient approximation

$$g = 1 - 0\cdot321\mu^{\frac{1}{2}}\sigma(0\cdot376\mathring{a}\mu^{\frac{1}{2}}) + s_2''m_2/m_1 \quad . \quad . \quad . \quad . \quad (17)$$

from which, by comparison with equation (13), we see that $b\mu = s_2''m_2/m_1$; and, since $m_1 = 10\cdot20$ and at the higher concentrations $\mu \sim 2m$, $2b = s_2''/10\cdot20$, and the value of $b = 0\cdot1$, $0\cdot2$, $0\cdot3$, and $0\cdot45$ correspond to total solvation numbers of 2, 4, 6, and 9 respectively. Then if we make the assumption that the hydrogen sulphate ion is not solvated (Part XI, *loc. cit.*) and remember that each mole of metal sulphate produces two moles of cations, we obtain approximate solvation numbers of 1, 2, 3, 3, and 4·5 for the ammonium, cæsium, lithium, potassium, and sodium ions respectively.

The value of the distance of closest approach $\mathring{a}$ obtained for electrolytes in aqueous solution is generally between 3 and 5 Å, but the value of $\mathring{a} = 10$ that we have obtained is reasonable as it is to a good approximation equal to the calculated values for the various electrolytes if their cations each have one complete solvation shell. We may calculate

from the molal volume of sulphuric acid of 54 c.c. (Part XI, *loc. cit.*) that the mean radius of a sulphuric acid molecule is 2·9 Å. We may to a good approximation take this value also for the mean radius of the hydrogen sulphate ion. If r^+ is the radius of the cation, r^- the radius of the hydrogen sulphate ion, and d the diameter of a sulphuric acid molecule, then the distance of closest approach of a hydrogen sulphate ion and a cation with one complete solvation layer is then given by $å = r^+ + r^- + d$. Values of the distance of closest approach calculated in this way are given in the annexed Table. It may be seen that the calculated values of $å$ are all of the order of 10 Å.

Electrolyte	r^+ (Å)	r^- (Å)	d (Å)	$å = (r^+ + r^- + d)$ (Å)
LiHSO$_4$	0·60	2·90	5·80	9·3
NaHSO$_4$	0·95	,,	,,	9·7
KHSO$_4$	1·33	,,	,,	10·0
NH$_4$HSO$_4$	1·48	,,	,,	10·2
CsHSO$_4$	1·69	,,	,,	10·4

The order of increasing osmotic coefficients at any given concentration, and hence of ionic solvation, is $NH_4^+ < Cs^+ < K^+ \sim Li^+ < Na^+$, which is the order to be expected from the size of the ions, except for the anomalous position of lithium. This order of increasing solvation is the same as the order found by viscosity and density measurements in sulphuric acid (Part XI, *loc. cit.*), except that from these results the solvation number of lithium seemed to be closer to that of sodium than to that of potassium. It is interesting to note that the radius ratio of the lithium ion and a sulphuric acid molecule is such that the co-ordination number of lithium is only three. This may account for the fact that its solvation number is approximately three whereas because of its smaller size and hence more intense electric field (compared with that of sodium) it would be expected to have a larger solvation number than sodium. The co-ordination numbers, approximate solvation numbers, and radius ratios for the various cations are given in the following Table :

Cation	Solvation no.	Co-ordination no.	$r^+/r_{H_2SO_4}$
Li$^+$	3	3	0·207
Na$^+$	4·5	4	0·327
K$^+$	3	6	0·458
Cs$^+$	2	6	0·583
NH$_4^+$	1	6	0·510

Thus it appears that Li$^+$ and Na$^+$ both have complete solvation shells but that those of K$^+$, Cs$^+$, and NH$_4^+$ are incomplete.

Incomplete Dissociation of Silver and Thallous Sulphates.—The results obtained with silver and thallous sulphates are of special interest in that the osmotic coefficients of their solutions decrease with increasing concentration over the whole range studied, and can only be fitted to equation (13) with a value of $å$ less than 10. The results for both thallium and silver can be fitted approximately by taking $å = 8$ and $b = 0$. These values are, however, inconsistent, as for the unsolvated ions we should expect a distance of closest approach for silver and thallium of 4·2 and 4·3 Å respectively. Now there is much evidence that many silver and thallous salts are incompletely dissociated in water, probably because of covalent-bond formation between the anion and the cation, and it does not seem unlikely therefore that the apparently small $å$ value is due to incomplete dissociation. This incomplete dissociation is presumably due to covalent bonding rather than to ion-pair formation, as both the observed distance of closest approach and those calculated for unsolvated ions are greater than the Bjerrum critical distance

$$q = \frac{|z_1 z_2| e^2}{2\varepsilon kT} = 2\cdot56 \text{ Å}$$

taking $\varepsilon = 115$, $T = 283\cdot5°$ K, and $z_1 = z_2 = 1$. In fact, it appears that because of the high dielectric constant of sulphuric acid and the relatively large size of the hydrogen sulphate ion, it is impossible for any univalent metal hydrogen sulphate to form ion-pairs in sulphuric acid.

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