167. *Solutions in Sulphuric Acid. Part XXVII.* The Self-dissociation Equilibria of Sulphuric Acid: Values of the Equilibrium Constants at* 10°.

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New values of the equilibrium constants for the self-dissociation equilibria of sulphuric acid at 10° are obtained from new freezing points of solutions of water, disulphuric acid, and metal hydrogen sulphates reported in the preceding paper. An improved method of calculation is used which, unlike earlier calculations, makes allowance for the non-ideality of the solutions and the interdependence of the various self-dissociation equilibria.

A simple method is described of allowing for the concentrations of the self-dissociation species in the calculation of ν-values for complex electrolytes in sulphuric acid.

Because of the appreciable self-dissociation of sulphuric acid, solutions of electrolytes in this solvent always contain at least small concentrations of ions and molecules resulting from the solvent dissociation, in addition to those from the electrolyte. To interpret quantitatively the properties of electrolyte solutions, such as their freezing points and electrical conductivities, it is necessary to know in detail the nature and extent of the self-dissociation. In this paper new values of the equilibrium constants of the self-dissociation reactions of sulphuric acid at 10° are derived.

The primary dissociation of sulphuric acid is into water and disulphuric acid:

$$2H_2SO_4 \rightleftharpoons H_2O + H_2S_2O_7 \quad . \ . \ . \ . \ . \ . \ . \quad (i)$$

and earlier work [1] has shown that both these products undergo ionisation according to the equations:

$$H_2O + H_2SO_4 \rightleftharpoons H_3O^+ + HSO_4^- \quad . \ . \ . \ . \quad (ii)$$

$$H_2S_2O_7 + H_2SO_4 \rightleftharpoons H_3SO_4^+ + HS_2O_7^- \quad . \ . \ . \ . \quad (iii)$$

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* Part XXVI, preceding paper.

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

In addition, the ions $H_3SO_4^+$ and HSO_4^- are in equilibrium as a result of the autoprotolysis or proton-transfer reaction of the solvent:

$$2H_2SO_4 \rightleftharpoons H_3SO_4^+ + HSO_4^- \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(iv)}$$

Consequently the ions H_3O^+ and $HS_2O_7^-$ are also in equilibrium in what has been called the ionic self-dehydration reaction:[2]

$$2H_2SO_4 \rightleftharpoons H_3O^+ + HS_2O_7^- \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(v)}$$

Only four of these equilibria are independent, and the self-dissociation of sulphuric acid may be completely and conveniently described by the equilibrium constants (1)—(4) of reactions (ii)—(v):

$$K_b = [H_3O^+][HSO_4^-]/[H_2O] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$K_a = [H_3SO_4^+][HS_2O_7^-]/[H_2S_2O_7] \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$K_{ap} = [H_3SO_4^+][HSO_4^-] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

$$K_{id} = [H_3O^+][HS_2O_7^-] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Values of $K_{ap} = 1{\cdot}7 \times 10^{-4}$ mole² kg.⁻², of $K_{id} = 7 \times 10^{-5}$ mole² kg.⁻², of $K_a = 2 \times 10^{-2}$ mole kg.⁻¹, and of $K_b = 1{\cdot}2$ mole kg.⁻¹ have been given in Parts I,[3] II,[1] and IV[2] of this series. The constants K_{ap} and K_{id} were determined by assuming that reactions (ii) and (iii) proceed essentially to completion, *i.e.*, $K_a = K_b = \infty$: in this case, reactions (iv) and (v) are independent, and only (iv) will be repressed in solutions of metal hydrogen sulphates or other simple bases:

$$B + H_2SO_4 \longrightarrow BH^+ + HSO_4^- \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(vi)}$$

while both reactions (iv) and (v) will be repressed in solutions of water. This distinction formed the basis of the method by which K_{ap} and K_{id} were determined. It is, however, rather a poor assumption to put $K_a = \infty$, and thus the values given above for K_{ap} and K_{id} can be only approximate. The assumption of ideality of the solutions, and errors in the experimental data, also limit the accuracy of these values. In the present paper new values for the equilibrium constants of the self-dissociation reactions are obtained by using the accurate freezing points reported in Part XXVI[4] and as far as possible eliminating the assumptions made in the earlier work. The method used was essentially one of trial and error, in which the first step was to calculate the concentrations of all the species in solutions of water, disulphuric acid, and metal sulphates, for different assumed values of the equilibrium constants of the self-dissociations. The osmotic coefficients of the solutions were then calculated from the total concentration of solute species at rounded stoicheiometric concentrations, and a comparison of these values with theoretical values of the osmotic coefficients enabled " best values " of the various equilibrium constants to be selected. These values are given in Table 1.

TABLE 1. *Equilibrium constants for the self-dissociation reactions of sulphuric acid at* 10°.

$K_{ap} = [H_3SO_4^+][HSO_4^-] = 1{\cdot}7 \times 10^{-4}$ mole² kg.⁻².
$K_{id} = [H_3O^+][HS_2O_7^-] = 3{\cdot}5 \times 10^{-5}$ mole² kg.⁻².
$K_a = [H_3SO_4^+][HS_2O_7^-]/[H_2S_2O_7] = 1{\cdot}4 \times 10^{-2}$ mole kg.⁻¹.
$K_b = [H_3O^+][HSO_4^-]/[H_2O] = 1$ mole kg.⁻¹.

Symbolism.—Concentrations in this paper are expressed in molal units (m) (moles of solute per kg. of solvent). In some cases, in order to avoid the excessive use of subscripts the symbol [A] is used in place of m_A, and both denote the *molal* concentration of species A. Stoicheiometric molalities are denoted by the symbol m^s. It is also convenient to distinguish between the total concentrations of ionic and non-ionic solute species. The total

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[2] Gillespie, *J.*, 1950, 2516.
[3] Gillespie, Hughes, and Ingold, *J.*, 1950, 2473.
[4] Bass and Gillespie, preceding paper.

molality of the former is denoted by Σm_i, and of the latter by Σm_j, while Σm_{ij} denotes the total molal concentration of all solute species, both ionic and non-ionic.

Calculation of the Concentrations of Self-dissociation Species.—For given values of the dissociation constants (1)—(4) the concentrations of all the species present in solutions of an electrolyte in sulphuric acid may be calculated. It is difficult to express the concentrations of each of the solute species in terms of the stoicheiometric concentration of the added electrolyte; however, it is simple to express the concentration of any of these species in terms of one of the others and one or more of the equilibrium constants (1)—(4). The method used was to select suitable values of $[H_3SO_4^+]$, and to calculate corresponding values of $[HSO_4^-]$ from the value of K_{ap} given in Table 1. Calculation of the remaining concentrations of species then depends on the mode of ionisation of the particular solute to be considered.

(a) *Water and disulphuric acid.* The condition for electrical neutrality gives the relation:

$$[HSO_4^-] - [H_3SO_4^+] = [H_3O^+] - [HS_2O_7^-] = a \quad . \quad . \quad . \quad (5)$$

From (4) and (5) it follows that

$$[H_3O^+] = \tfrac{1}{2}a + \tfrac{1}{2}(a^2 + 4K_{id})^{\frac{1}{2}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

Then $[HS_2O_7^-]$ can be obtained from expression (4), $[H_2S_2O_7]$ from (2), and $[H_2O]$ from (1). The corresponding stoicheiometric concentration of water or disulphuric acid is given by:

$$m^s\,(H_2O \text{ or } H_2S_2O_7) = \pm\{[H_2O] + [H_3O^+] - [H_2S_2O_7] - [HS_2O_7^-]\} \quad . \quad (7)$$

(b) *Bases.* It is convenient to deal first with the case of a simple base of the sulphuric acid system, *i.e.*, a base which ionises to give only the hydrogen sulphate ion and a corresponding cation (equation vi).

For all concentrations of base we have:

$$[H_2O] + [H_3O^+] = [HS_2O_7^-] + [H_2S_2O_7] \quad . \quad . \quad . \quad . \quad (8)$$

From (1), (2), (4), and (8), we find:

$$[H_3O^+] = \{K_{id}(1 + [H_3SO_4^+]/K_a)/(1 + [HSO_4^-)/K_b)\}^{\frac{1}{2}} \quad . \quad . \quad . \quad (9)$$

$[HS_2O_7^-]$ can then be obtained from (4), and $[BH^+]$ from the condition for electrical neutrality, namely:

$$[BH^+] + [H_3SO_4^+] + [H_3O^+] = [HSO_4^-] + [HS_2O_7^-] \quad . \quad . \quad (10)$$

The concentration of base, [B], can be obtained from the equilibrium constant for the ionisation of the base:

$$K_B = [BH^+][HSO_4^-]/[B] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

Finally, the stoicometric concentration of the base is given by:

$$m_B{}^s = [B] + [BH^+] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

For fully ionised bases, and in particular for metal hydrogen sulphates, we have:

$$MHSO_4 \longrightarrow M^+ + HSO_4^- \quad . \quad . \quad . \quad . \quad . \quad . \quad (vii)$$

$$m_B{}^s = [BH^+] = [M^+] = m^s{}_{MHSO_4} \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

(c) *Acids.* Similarly it is convenient to discuss the case of a simple acid of the sulphuric acid system, *i.e.*, a substance which ionises to give only the sulphuric acidium ion and a corresponding anion:

$$HA + H_2SO_4 \rightleftharpoons H_3SO_4^+ + A^- \quad . \quad . \quad . \quad . \quad . \quad (viii)$$

Values of $[H_3O^+]$ and $[HS_2O_7^-]$ can be obtained from expressions (9) and (4) respectively, and then $[A^-]$ can be obtained from the condition for electrical neutrality:

$$[H_3SO_4^+] + [H_3O^+] = [HS_2O_7^-] + [HSO_4^-] + [A^-] \quad . \quad . \quad (14)$$

Finally HA can be found from the equilibrium constant for the ionisation of the acid:

$$K_{HA} = [H_3SO_4^+][A^-]/[HA] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

(d) *Complex electrolytes.* We use the term complex electrolyte to denote any solute except water or disulphuric acid which when dissolved in sulphuric acid gives rise to both $H_3SO_4^+$ or HSO_4^- ions, and H_3O^+ or $HS_2O_7^-$ ions, simultaneously. The most common electrolytes of this type ionise to give H_3O^+ and HSO_4^-, *e.g.*:

$$XOH + 2H_2SO_4 = X^+ + H_3O^+ + 2HSO_4^- \quad . \quad . \quad . \quad . \quad (ix)$$

and $$H_3BO_3 + 6H_2SO_4 = 3H_3O^+ + B(HSO_4)_4^- + 2HSO_4^- \quad . \quad . \quad . \quad (x)$$

In all cases the concentrations of all the species in the system are easily obtained by solving equations (1)—(4), together with two other equations, one of which expresses the composition of the solution and the other the condition for electrical neutrality. Thus in the case of XOH, assumed to be fully ionised, the condition for electrical neutrality gives:

$$[HSO_4^-] - [H_3SO_4^+] = [X^+] + [H_3O^+] - [HS_2O_7^-] = a \quad . \quad . \quad (16)$$

and the stoicheiometric composition of any solution is given by:

$$m^s{}_{XOH} = [X^+] = [H_2O] + [H_3O^+] - [H_2S_2O_7] - [HS_2O_7^-] \quad . \quad . \quad (17)$$

From equations (1)—(4) and (16) and (17) it follows that:

$$[H_3O^+] = \frac{a \pm \{a^2 + 4([HSO_4^-]/K_b + 2)([H_3SO_4^+]/K_a + 2)K_{id}\}^{\frac{1}{2}}}{2(2 + [HSO_4^-]/K_b)} \quad . \quad (18)$$

or, if we assume that water is fully ionised, then:

$$[H_3O^+] = \frac{a \pm \{a^2 + 8K_{id}([H_3SO_4^+]/K_a + 2)\}^{\frac{1}{2}}}{4} \quad . \quad . \quad . \quad (19)$$

Then $[HS_2O_7^-]$ may be found from equation (4). $[H_2S_2O_7]$ is obtained from equation (2), and hence $[X^+]$ from (16).

In each case Σm_{ij}, the total concentration of all solute species, can be found by summation, *i.e*:

$$\begin{aligned}\Sigma m_{ij} = {} & [H_3SO_4^+] + [HSO_4^-] + [H_3O^+] + [HS_2O_7^-] + [H_2S_2O_7] \\ & + [H_2O] + \{([BH^+] + [B]) \text{ or } - ([HA] + A^-])\} \quad . \quad (20)\end{aligned}$$

The total concentration of all the ionic species is given by:

$$\Sigma m_i = [H_3SO_4^+] + [HSO_4^-] + [H_3O^+] + [HS_2O_7^-] + ([BH^+] \text{ or } [A^-]) \quad . \quad (21)$$

It is convenient to have values of Σm_{ij} and Σm_i at round molal concentrations (m^s) of added electrolyte, and these were obtained by interpolation. Tables 2—7 give such values for water, disulphuric acid, a strong base B, a strong acid HA, and the complex electrolyte XOH. They were calculated by using the final values of the dissociation constants given in Table 1. Values for weak bases and weak acids can be readily obtained from the values for the strong electrolytes by making use of the appropriate dissociation constant for the particular base or acid. When obtaining these values by the method described it was necessary to calculate similar tables of concentrations of solute species for each of the sets of trial values of the equilibrium constants that were considered. Fig. 1 shows how the

TABLE 2. *Concentrations of species in solutions of a metal hydrogen sulphate or other strong base.*

m^s ($MHSO_4$) or m^s (B)	$[H_3SO_4^+]$	$[HSO_4^-]$	$[H_3O^+]$	$[HS_2O_7^-]$	$[H_2S_2O_7]$	$[H_2O]$	Σm_{ij}	Σm_i
0·000	0·0113	0·0150	0·0080	0·0044	0·0036	0·0001	0·0424	0·03
0·005	0·0096	0·0177	0·0076	0·0046	0·0031	0·0001	0·0477	0·04875
0·010	0·0082	0·0209	0·0074	0·0047	0·0028	0·0001	0·0541	0·05412
0·015	0·0070	0·0243	0·0072	0·0048	0·0025	0·0002	0·0610	0·0583
0·020	0·0061	0·0281	0·0070	0·0049	0·0022	0·0002	0·0686	0·0662
0·025	0·0053	0·0321	0·0068	0·0050	0·0020	0·0002	0·0766	0·0744
0·030	0·0047	0·0363	0·0067	0·0051	0·0018	0·0002	0·0849	0·0829
0·035	0·0042	0·0406	0·0066	0·0052	0·0016	0·0002	0·0935	0·0917
0·040	0·0038	0·0450	0·0065	0·0053	0·0015	0·0003	0·1024	0·1006
0·05	0·0032	0·0543	0·0064	0·0054	0·0012	0·0003	0·1208	0·1193
0·06	0·0027	0·0636	0·0062	0·0055	0·0011	0·0004	0·1395	0·1380
0·07	0·0023	0·0730	0·0062	0·0056	0·0009	0·0004	0·1584	0·1571
0·08	0·0021	0·0825	0·0061	0·0057	0·0008	0·0004	0·1775	0·1763
0·09	0·0018	0·0923	0·0060	0·0058	0·0008	0·0005	0·1972	0·1959
0·10	0·0017	0·1019	0·0060	0·0058	0·0007	0·0006	0·2167	0·2154
0·12	0·0014	0·1214	0·0059	0·0059	0·0006	0·0007	0·2559	0·2546
0·14	0·0012	0·1411	0·0058	0·0060	0·0005	0·0008	0·2954	0·2941
0·16	0·0010	0·1607	0·0057	0·0061	0·0005	0·0009	0·3349	0·3335
0·18	0·0009	0·1803	0·0056	0·0061	0·0005	0·0010	0·3746	0·3731
0·20	0·0008	0·2002	0·0056	0·0062	0·0004	0·0011	0·4143	0·4128
0·24	0·0007	0·2396	0·0054	0·0064	0·0004	0·0013	0·4942	0·4925
0·28	0·0006	0·2793	0·0053	0·0066	0·0003	0·0015	0·5736	0·5718

TABLE 3. *Concentrations of species in water solutions* ($K_b = \infty$).

m^s (H_2O)	$[H_3SO_4^+]$	$[HSO_4^-]$	$[H_3O^+]$	$[HS_2O_7^-]$	$[H_2S_2O_7]$	Σm_{ij}	Σm_i
0·000	0·0113	0·0150	0·0080	0·0044	0·0036	0·0424	0·0387
0·005	0·0098	0·0172	0·0104	0·0032	0·0024	0·0431	0·0407
0·010	0·0085	0·0201	0·0140	0·0025	0·0016	0·0467	0·0451
0·015	0·0073	0·0235	0·0181	0·0020	0·0011	0·0516	0·0505
0·020	0·0063	0·0269	0·0224	0·0016	0·0007	0·0577	0·0570
0·025	0·0055	0·0309	0·0267	0·0013	0·0005	0·0649	0·0644
0·030	0·0048	0·0352	0·0315	0·0011	0·0004	0·0730	0·0726
0·04	0·0038	0·0440	0·0410	0·0008	0·0002	0·0898	0·0896
0·06	0·0026	0·0630	0·0607	0·0006	0·0001	0·1270	0·1269
0·08	0·0021	0·0822	0·0805	0·0004	—	0·1652	0·1652
0·10	0·0017	0·1017	0·1004	0·0004	—	0·2042	0·2042
0·12	0·0014	0·1214	0·1203	0·0003	—	0·2434	0·2434
0·14	0·0012	0·1412	0·1403	0·0003	—	0·2830	0·2830
0·16	0·0011	0·1611	0·1602	0·0002	—	0·3226	0·3226
0·18	0·0009	0·1809	0·1802	0·0002	—	0·3622	0·3622
0·20	0·0008	0·2008	0·2002	0·0001	—	0·4020	0·4020
0·24	0·0007	0·2407	0·2401	0·0001	—	0·4816	0·4816
0·28	0·0006	0·2806	0·2800	—	—	0·5612	0·5612
0·32	0·0005	0·3205	0·3200	—	—	0·6410	0·6410
0·36	0·0005	0·3605	0·3600	—	—	0·7210	0·7210
0·40	0·0004	0·4004	0·4000	—	—	0·8008	0·8008

TABLE 4. *Concentrations of species in water solutions* ($K_b = 1$).

m^s (H_2O)	$[H_3SO_4^+]$	$[HSO_4^-]$	$[H_3O^+]$	$[HS_2O_7^-]$	$[H_2O]$	$[H_2S_2O_7]$	Σm_{ij}	Σm_i
0·000	0·0113	0·0150	0·0080	0·0044	0·0001	0·0036	0·0424	0·0387
0·005	0·0100	0·0171	0·0107	0·0033	0·0001	0·0024	0·0435	0·0410
0·010	0·0086	0·0199	0·0140	0·0026	0·0002	0·0076	0·0468	0·0450
0·015	0·0074	0·0229	0·0178	0·0020	0·0004	0·0010	0·0617	0·0502
0·020	0·0064	0·0265	0·0220	0·0016	0·0006	0·0008	0·0577	0·0563
0·025	0·0056	0·0305	0·0262	0·0013	0·0008	0·0006	0·0649	0·0635
0·030	0·0050	0·0343	0·0305	0·0011	0·0011	0·0004	0·0725	0·0710
0·04	0·0040	0·0425	0·0394	0·0009	0·0017	0·0002	0·0887	0·0868
0·06	0·0029	0·0595	0·0573	0·0006	0·0035	0·0001	0·1239	0·1203
0·08	0·0023	0·0765	0·0748	0·0004	0·0057	0·0001	0·1596	0·1538
0·10	0·0018	0·0933	0·0919	0·0004	0·0085	0·0001	0·1960	0·1874
0·12	0·0015	0·1098	0·1084	0·0004	0·0120	—	0·2321	0·2201
0·14	0·0013	0·1257	0·1243	0·0003	0·0159	—	0·2674	0·2515
0·16	0·0012	0·1413	0·1403	0·0003	0·0199	—	0·3023	0·2824
0·18	0·0011	0·1565	0·1557	0·0003	0·0245	—	0·3380	0·3135
0·20	0·0010	0·1715	0·1707	0·0003	0·0294	—	0·3727	0·3433
0·24	0·0008	0·2008	0·2001	0·0002	0·0401	—	0·4418	0·4019
0·28	0·0007	0·2283	0·2277	0·0001	0·0523	—	0·5090	0·4567

TABLE 5. *Concentrations of species in oleum solutions.*

m^s ($H_2S_2O_7$)	[$H_3SO_4^+$]	[HSO_4^-]	[H_3O^+]	[$HS_2O_7^-$]	[$H_2S_2O_7$]	Σm_{ij}	Σm_i	ϕ
0·000	0·0113	0·0150	0·0080	0·0045	0·0036	0·0424	0·0387	0·980
0·005	0·0129	0·0131	0·0060	0·0058	0·0053	0·0431	0·0378	0·981
0·010	0·0144	0·0118	0·0047	0·0075	0·0072	0·0456	0·0384	0·982
0·015	0·0158	0·0108	0·0039	0·0089	0·0100	0·0492	0·0392	0·983
0·020	0·0171	0·0099	0·0033	0·0105	0·0128	0·0536	0·0408	0·980
0·025	0·0185	0·0091	0·0029	0·0123	0·0156	0·0584	0·0428	0·982
0·030	0·0199	0·0086	0·0025	0·0138	0·0186	0·0634	0·0448	0·981
0·04	0·0220	0·0078	0·0021	0·0163	0·0256	0·0738	0·0482	0·981
0·06	0·0263	0·0065	0·0016	0·0214	0·0402	0·0960	0·0558	0·981
0·08	0·0302	0·0056	0·0013	0·0259	0·0558	0·1188	0·0630	0·982
0·10	0·0335	0·0050	0·0012	0·0297	0·0711	0·1395	0·0684	0·989
0·12	0·0368	0·0046	0·0011	0·0333	0·0875	0·1633	0·0758	0·991
0·14	0·0399	0·0043	0·0010	0·0366	0·1043	0·1861	0·0818	0·990
0·16	0·0428	0·0040	0·0009	0·0397	0·1213	0·2077	0·0864	0·993
0·18	0·0455	0·0037	0·0008	0·0426	0·1385	0·2311	0·0926	0·990
0·20	0·0480	0·0035	0·0008	0·0453	0·1553	0·2529	0·0976	0·992

TABLE 6. *Concentrations of species in solutions of a strong acid.*

m^s (HA)	[$H_3SO_4^+$]	[HSO_4^-]	[H_3O^+]	[$HS_2O_7^-$]	[$H_2S_2O_7$]	Σm_{ij}	Σm_i
0·000	0·0113	0·0150	0·0080	0·0044	0·0036	0·0424	0·0387
0·005	0·0135	0·0126	0·0083	0·0042	0·0041	0·0477	0·0436
0·010	0·0159	0·0106	0·0087	0·0040	0·0047	0·0539	0·0492
0·015	0·0188	0·0090	0·0091	0·0038	0·0053	0·0610	0·0557
0·020	0·0219	0·0077	0·0095	0·0037	0·0058	0·0686	0·0628
0·025	0·0252	0·0066	0·0099	0·0035	0·0064	0·0766	0·0702
0·030	0·0289	0·0059	0·0104	0·0034	0·0070	0·0856	0·0786
0·040	0·0367	0·0047	0·0112	0·0032	0·0080	0·1038	0·0958
0·060	0·0530	0·0032	0·0129	0·0027	0·0102	0·1420	0·1338
0·080	0·0701	0·0022	0·0145	0·0024	0·0121	0·1813	0·1592
0·100	0·0882	0·0019	0·0159	0·0022	0·0137	0·2219	0·2082
0·120	0·1063	0·0016	0·0173	0·0020	0·0153	0·2625	0·2472
0·140	0·1247	0·0014	0·0186	0·0019	0·0167	0·3033	0·2866
0·160	0·1432	0·0012	0·0198	0·0018	0·0180	0·3440	0·3260
0·180	0·1617	0·0010	0·0210	0·0017	0·0193	0·3847	0·3654
0·200	0·1801	0·0009	0·0223	0·0015	0·0208	0·4256	0·4048
0·240	0·2181	0·0008	0·0241	0·0014	0·0227	0·5071	0·4744
0·280	0·2557	0·0007	0·0260	0·0013	0·0247	0·5884	0·5637
0·320	0·2941	0·0006	0·0277	0·0012	0·0265	0·6701	0·6436
0·360	0·3323	0·0005	0·0294	0·0012	0·0282	0·7516	0·7234
0·400	0·3706	0·0005	0·0310	0·0011	0·0299	0·8331	0·8032

TABLE 7. *Concentration of species in solutions of the complex electrolyte* XOH ($XOH + 2H_2SO_4 = X^+ + H_3O^+ + 2HSO_4^-$).

m^s (XOH)	[$H_3SO_4^+$]	[HSO_4^-]	[H_3O^+]	[$HS_2O_7^-$]	[$H_2S_2O_7$]	Σm_{ij}	Σm_i
0·000	0·0113	0·0150	0·0080	0·0045	0·0035	0·0424	0·0387
0·005	0·0084	0·0203	0·0103	0·0034	0·0019	0·0493	0·0474
0·010	0·0063	0·0273	0·0139	0·0026	0·0012	0·0613	0·0601
0·015	0·0048	0·0354	0·0177	0·0020	0·0007	0·0756	0·0749
0·02	0·0038	0·0450	0·0219	0·0016	0·0003	0·0926	0·0923
0·03	0·0027	0·0630	0·0314	0·0012	0·0002	0·1285	0·1283
0·04	0·0021	0·0822	0·0409	0·0009	0·0000	0·1661	0·1661
0·05	0·0017	0·1017	0·0507	0·0007	—	0·2048	0·2048
0·06	0·0014	0·1214	0·0606	0·0006	—	0·2440	0·2440
0·07	0·0012	0·1412	0·0705	0·0005	—	0·2834	0·2834
0·08	0·0011	0·1611	0·0804	0·0004	—	0·3230	0·3230
0·09	0·0009	0·1809	0·0904	0·0004	—	0·3626	0·3626
0·10	0·0008	0·2008	0·1003	0·0004	—	0·4023	0·4023
0·12	0·0007	0·2407	0·1203	0·0003	—	0·4820	0·4820
0·14	0·0006	0·2806	0·1402	0·0003	—	0·5617	0·5617
0·16	0·0005	0·3205	0·1602	0·0002	—	0·6414	0·6414
0·18	0·0005	0·3605	0·1802	0·0002	—	0·7214	0·7214
0·20	0·0004	0·4004	0·2002	0·0002	—	0·8012	0·8012

concentrations of the self-dissociation species (except HSO_4^-) change in solutions of a strong base B.

Osmotic Coefficients of Electrolyte Solutions.—For a dissociated solvent such as sulphuric acid it is convenient to let the standard state of the solvent be the pure hypothetical undissociated solvent. We shall denote all quantities relating to this standard state by a subscript asterisk, *e.g.*, T_*, ΔH^f_*, etc., and all quantities relating to the pure solvent containing the equilibrium concentrations of self-dissociation products by the subscript 0, *e.g.*, T_0, ΔH^f_0, etc. Then the activity of the solvent, a_1, in any solution is given by

$$\ln a_1 = [-\Delta H^f_*\theta + (\Delta H^f_*/T_* - \Delta C_p/2)\theta^2 \cdots]/\boldsymbol{R}T_*^2 \quad . \quad . \quad . \quad (22)$$

where θ is the freezing-point depression of the solute calculated from the freezing point T_* of the hypothetical undissociated solvent, *i.e.*, $\theta = T_* - T$, where T is the freezing point of the solution, ΔH^f_* is the heat of fusion of the undissociated solvent at the temperature T_*, and ΔC_p is the difference in the heat capacities of the solid and the liquid solvent. The molal osmotic coefficient, ϕ,† of the solvent may be defined by:

$$\ln a_1 = -\phi\Sigma m_{ij}/M \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (23)$$

where M is the number of moles of solvent in 1 kg. of solvent, and Σm_{ij} is the total concentration of all the solute species in solution,

i.e.,
$$\Sigma m_{ij} = \nu m^s + m_d \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (24)$$

where m^s is the stoicheiometric concentration of solute, ν the number of moles of particles (molecules and ions) produced in the solution by one mole of the solute, and m_d is the total molality of the products of the solvent self-dissociation.

The cryoscopic constant k_* of the undissociated solvent may be defined by the relation:

$$k_* = \boldsymbol{R}T^2/M\Delta H^f_* \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (25)$$

From (22), (23), and (25), we have:

$$\phi = \theta(1 + \beta\theta)/k_*\Sigma m_{ij} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (26)$$

where $\beta = (1/T_* - \Delta C_p/2\Delta H^f_*)$.

The cryoscopic constant is usually defined by the equation:

$$k_0 = \boldsymbol{R}T_0^2/M\Delta H^f_0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (27)$$

which for sulphuric acid has been shown [6] to have the value of 6·12.

The relation between ΔH^f_* and ΔH^f_0 is:

$$\Delta H^f_0 = \Delta H^f_* + \alpha\Delta H_d$$

where ΔH_d is the heat of self-dissociation, and α is the degree of self-dissociation. The value of $\alpha\Delta H_d$ is discussed in a later paper in detail; it is approximately 7 cal. mole^{-1}, which is only slightly greater than the experimental error ($\pm$3 cal. mole^{-1}) in the heat of fusion [7] ($\Delta H^f_0 = 2560$ cal. mole^{-1}) and can be neglected without appreciable error. Since also T_* (283·78° K), differs only slightly from T_0 (283·52° K), we may conclude that

$$k_* = k_0 = 6{\cdot}12 \pm 0{\cdot}02$$

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† The molal osmotic coefficient, ϕ, is used in this paper rather than the rational osmotic coefficient, g, which was used in Part XVII,[5] because it is somewhat easier to calculate, and because it is more commonly used in, for example, the discussion of aqueous solutions. The relation between g and ϕ is $\phi \approx g(1 - \Sigma m_{ij}/2M)$, and the difference is small at the concentrations with which we are concerned.

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

[6] Gillespie, *J.*, 1954, 1851.

[7] Rubin and Giauque, *J. Amer. Chem. Soc.*, 1952, **74**, 800.

In earlier papers of this series [3,6] the cryoscopic constant was denoted by k_f. When, as in the present case, the difference between k_* and k_0 can be neglected it is proposed to omit the subscripts and to use the symbol k. The value of β may be computed [5] to be 0·002. Thus equation (26) may be written:

$$\phi = \theta(1 + 0{\cdot}002\theta)/6{\cdot}12\Sigma m_{ij} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (28)$$

Theoretical Osmotic Coefficients.—The contribution of electrostatic interionic forces to the osmotic coefficient of an electrolyte solution is given by the Debye–Hückel theory which leads to the equation:

$$\phi^{\text{el}} = \frac{2{\cdot}303}{3} A|z_+z_-| \frac{c}{m\rho} I^{\frac{1}{2}}\sigma(x) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (29)$$

where $x = B\mathring{a}I^{\frac{1}{2}}$, $\sigma(x) = 3/x^3[(1 + x) - 2 \ln (1 + x) - 1/(1 + x)]$

$$A = \left(\frac{2\pi N}{1000}\right)^{\frac{1}{2}} \cdot \frac{e^3}{2{\cdot}303(\varepsilon kT)^{2/3}};\ 10^8B = \left(\frac{8\pi Ne^2}{1000\varepsilon kT}\right)^{\frac{1}{2}},$$

c is the molar concentration of the electrolyte and m its molal concentration, I is the ionic strength $= \frac{1}{2}c(\nu_+z_+^2 + \nu_-z_-^2)$, ν_+ and ν_- are the numbers of moles of cations and anions respectively produced by one mole of electrolyte, z_+ and z_- are the valencies of the cations and anions respectively, ε is the dielectric constant, $\mathring{a}$ is the distance of closest approach of the cation and anion, and ρ is the density of the solution. The value of ε is not quite certain. Gillespie and Oubridge [5] used $\varepsilon = 115$, but from their own results and those of Brand, James, and Rutherford,[8] and of Gillespie and Cole,[9] Gillespie and White [10] recently deduced a value of 120 at 10° c. Substituting $\varepsilon = 120$, we find $A = 0{\cdot}291$, and $B = 0{\cdot}273$. For an electrolyte $MHSO_4$, $z_+ = z_- = 1$, therefore:

$$\phi^{\text{el}} = -0{\cdot}223I^{\frac{1}{2}} \cdot \frac{c}{m\rho}\,\sigma(0{\cdot}273\mathring{a}I^{\frac{1}{2}}) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (30)$$

This equation applies only to a solution of a single electrolyte and is therefore not strictly applicable to the solutions we are considering, which also contain appreciable concentrations of the ions resulting from the solvent self-dissociation. For simplicity we will assume that it is valid for our solutions if we calculate the ionic strength from the expression

$$I = \Sigma c_i z_i^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (31)$$

where c_i is the molar concentration of the ion i and z_i its valency, and where the summation is taken over all the ions in the solution including those resulting from the solvent self-dissociation.

Hence, we obtain:

$$\phi = 1 + \phi^{\text{el}} = 1 - 0{\cdot}223I^{\frac{1}{2}} \cdot \frac{c}{m\rho} \cdot \sigma(0{\cdot}273\mathring{a}I^{\frac{1}{2}}) \quad . \quad . \quad . \quad . \quad (32)$$

As is discussed in the following paper (see also ref. 5), a value of $\mathring{a} = 10$ Å seems appropriate for most electrolyte solutions in sulphuric acid. In order to make some allowance for ionic solvation and other factors not allowed for by the Debye–Hückel theory, we may add an empirical term, $b\Sigma m_i$, where b is an arbitrary constant, thus:

$$\phi = 1 - 0{\cdot}223I^{\frac{1}{2}} \cdot \frac{c}{m\rho} \cdot \sigma(0{\cdot}273\mathring{a}I^{\frac{1}{2}}) + b\Sigma m_i \quad . \quad . \quad . \quad . \quad (33)$$

Molar concentrations, c, were obtained from the *molal* concentrations, m, by using the

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[8] Brand, James, and Rutherford, *J.*, 1953, 2447.

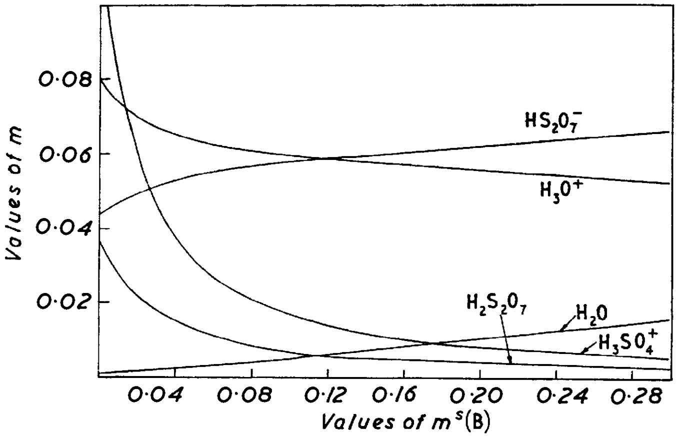
[9] Gillespie and Cole, *Trans. Faraday Soc.*, 1956. **52** 1325.

[10] Gillespie and White, *Trans. Faraday Soc.*, 1958, **54**, 1846.

appropriate density value. Densities were obtained from the earlier work of Gillespie and Wasif [11] or from the results of some new measurements given in a following paper.[12]

The Freezing Point (T_*) *of the Hypothetical Undissociated Solvent.*—The freezing-point depressions required in the present calculations have to be computed from the freezing point, T_*, of the hypothetical undissociated solvent. The freezing-point depression θ_0 produced by the products of the self-dissociation may be calculated from their concentration, m_d, by using the appropriate form of equation (28) which is $\theta_0 = 6{\cdot}12\phi_0 m_d$ (where the term $0{\cdot}002\theta$ has been justifiably neglected), if ϕ_0, the osmotic coefficient of the pure solvent, is known. There is no way of calculating ϕ_0 from experimental quantities and so some assumption must be made about its value. Initially it was simplest to assume that $\phi_0 = 1{\cdot}00$, but it became evident during the calculations that ϕ_0 must be less than 1·00. The Debye–Hückel limiting law gives a value of 0·95. Finally a value of 0·98 was chosen. The various theoretical curves which fit the experimental curves at higher concentrations give values in the range 0·97—0·99 at the value of $I^{\frac{1}{2}}$ corresponding to the pure solvent. It must be admitted that the choice of $\phi_0 = 0{\cdot}98$ is rather arbitrary and it could possibly be in error by as much as 0·01. Fortunately an error of this magnitude would make little difference to the osmotic coefficient curves except at the lowest concentrations, and affects none of the main conclusions of this and the following papers. For the values of K_{ap}, K_{id}, K_a, and K_b finally selected (Table 1), $m_d = 0{\cdot}0424$, hence $\theta_0 = 0{\cdot}254°$, and $T_* = 10{\cdot}625°$ C.

FIG. 1. *Concentrations of species in solutions of a strong base.*



Determination of the Equilibrium Constants of the Self-dissociation Reactions.—Values of $K_{ap} = 1{\cdot}7 \times 10^{-4}$ and $1{\cdot}56 \times 10^{-4}$ mole^2 kg.$^{-2}$ have been given previously,[3,5] and thus the range $1{\cdot}5 \times 10^{-4}$ to $1{\cdot}9 \times 10^{-4}$ was selected for the present calculations. Since the previous method of determining K_{id} assumed that disulphuric acid is fully ionised, it must have given a value, 7×10^{-5}, which was too high. Values in the range 1×10^{-5} to 7×10^{-5} mole^2 kg.$^{-2}$ were therefore chosen for the present calculation. Rather smaller freezing-point depressions for disulphuric acid solutions were obtained by the accurate equilibrium-method measurements described in the previous paper than in the earlier work. It was therefore expected that the previous value of $2{\cdot}0 \times 10^{-2}$ mole kg.$^{-1}$ for K_a would be rather too high, and values in the range 1·0—$2{\cdot}0 \times 10^{-2}$ were chosen for our calculations. Since the value of K_b is large, *i.e.*, the ionisation of water is almost complete, it is not necessary to know its value accurately. The earlier value of $K_b = 1{\cdot}2$ mole kg.$^{-1}$ was therefore rounded off to 1 mole kg.$^{-1}$ and used in all the calculations. This value was

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[11] Gillespie and Wasif, *J.*, 1953, 215.

[12] Flowers, Gillespie, and Robinson, *J.*, 1960, 845.

confirmed by the present work. In all cases, except when water itself is the solute, the difference between using this value and assuming that water is fully ionised is almost negligible.

The Autoprotolysis Constant.—The total number of combinations of all the values of the equilibrium constants to be considered was rather large, but fortunately K_{ap} could be determined more or less independently of K_{id}, K_a, and K_b. It may be seen from Table 2 and Fig. 1 that in solutions of metal hydrogen sulphates in sulphuric acid the concentrations of H_3O^+, H_2O, $HS_2O_7^-$, $H_2S_2O_7$, change rather slowly with increasing concentration of metal hydrogen sulphate, and the sum of their concentrations remains approximately constant. Thus the variation of Σm_{ij} and therefore of ϕ with $m^s{}_{MHSO_4}$ is to a first approximation independent of the concentrations of these ions, and therefore of the constants K_{id}, K_a, and K_b. It is possible therefore to use the freezing points of metal hydrogen sulphate solutions to determine K_{ap}, even although K_{id}, K_a, and K_b are not initially known with accuracy. Values of the concentrations of all the species in solutions of a metal hydrogen sulphate were calculated as described above, at rounded stoicheiometric concentrations of solute, m^s, for values of $K_{ap} = 1{\cdot}5$, 1·6, 1·7, 1·8, and $1{\cdot}9 \times 10^{-4}$. Then from the values of Σm_{ij} and the freezing-point depressions θ calculated from the experimental freezing points given in Part XXVI [4] values of ϕ were calculated by means of equation (28). Table 2 shows the concentrations of all the species in solutions of a metal hydrogen sulphate, and the total concentration Σm_{ij}, calculated on the basis of the constants $K_{ap} = 1{\cdot}7 \times 10^{-4}$, $K_{id} = 3{\cdot}5 \times 10^{-5}$, $K_a = 1{\cdot}4 \times 10^{-2}$, and $K_b = 1$. Table 8 gives the freezing-point depressions, and Table 9 the osmotic coefficients, for each of the electrolytes $NaHSO_4$, $KHSO_4$, and NH_4HSO_4. Similar tables were computed for each of the values of K_{ap} given above. Various other values of K_{id} and K_{ap} were used during preliminary calculations and it was found, as expected, that the effect on the values of the osmotic coefficients obtained was almost negligible. Fig. 2 shows a plot of values of ϕ against $I^{\frac{1}{2}}$ for each of the above three electrolytes and each of the values of $K_a = 1{\cdot}5$,

TABLE 8. *Freezing-point depressions for some electrolyte solutions.*

(Calculated from the hypothetical freezing-point of the undissociated acid $T_* = 10{\cdot}625°$.)

m^s $(MHSO_4)$	0·000	0·005	0·010	0·015	0·020	0·025	0·030	0·035	0·040	0·05	0·06	0·07
$KHSO_4$	0·254	0·286	0·324	0·365	0·411	0·460	0·510	0·563	0·616	0·723	0·840	0·955
$NaHSO_4$	0·254	0·286	0·324	0·366	0·412	0·461	0·512	0·564	0·619	0·730	0·846	0·961
NH_4HSO_4	0·254	0·286	0·323	0·364	0·410	0·459	0·508	0·558	0·610	0·720	0·832	0·946
H_3O,H_2SO_4	0·254	0·261	0·279	0·308	0·345	0·388	0·433	0·479	0·531	0·632	0·741	0·842
$H_2S_2O_7$	0·254	0·259	0·274	0·297	0·321	0·349	0·380	0·413	0·443	—	0·576	—

m^s $(MHSO_4)$	0·08	0·09	0·10	0·12	0·14	0·16	0·18	0·20	0·24	0·28	0·32	0·36
$KHSO_4$	1·070	1·190	1·309	1·546	1·789	2·035	2·280	2·524	3·024	—	—	—
$NaHSO_4$	1·079	1·198	1·321	1·569	1·827	2·082	2·342	2·603	3·167	3·677	—	—
NH_4HSO_4	1·059	1·178	1·293	1·525	1·759	1·993	2·225	2·459	—	—	—	—
H_3O,H_2SO_4	0·951	1·061	1·172	1·384	1·601	1·818	2·034	2·250	2·669	3·087	3·495	3·891
$H_2S_2O_7$	0·713	—	0·852	0·990	1·121	1·262	1·400	1·530	—	—	—	—

TABLE 9. *Osmotic coefficients ϕ of some metal hydrogen sulphate solutions.*

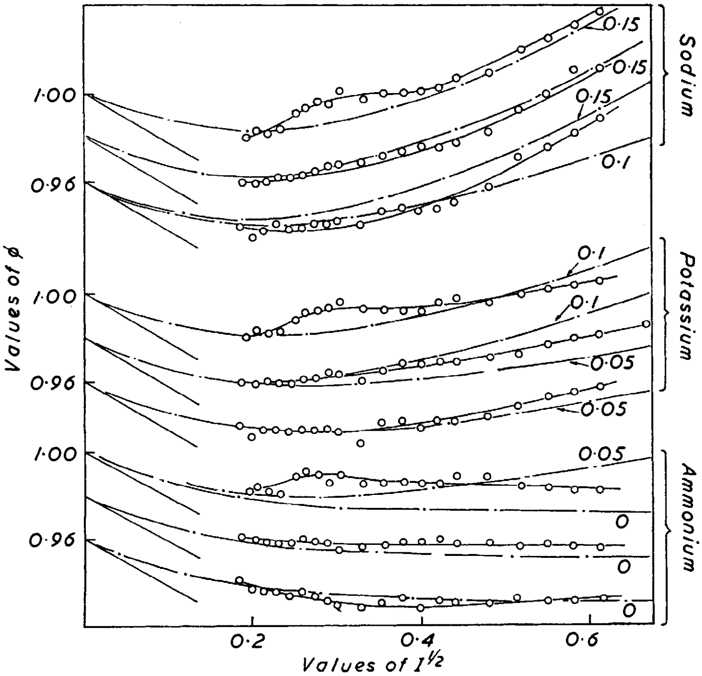
m^s $(MHSO_4)$	$I^{\frac{1}{2}}$ *	$KHSO_4$	$NaHSO_4$	NH_4HSO_4	m^s $(MHSO_4)$	$I^{\frac{1}{2}}$ *	$KHSO_4$	$NaHSO_4$	NH_4HSO_4
0·000	0·189	0·980	0·980	0·980	0·070	0·378	0·988	0·994	0·978
0·005	0·203	0·979	0·979	0·979	0·080	0·401	0·988	0·996	0·978
0·010	0·217	0·980	0·980	0·978	0·090	0·422	0·989	0·996	0·979
0·015	0·232	0·979	0·982	0·977	0·10	0·443	0·989	0·998	0·977
0·020	0·247	0·979	0·982	0·977	0·12	0·482	0·991	1·003	0·977
0·025	0·262	0·981	0·983	0·979	0·14	0·517	0·993	1·013	0·976
0·030	0·276	0·981	0·985	0·978	0·16	0·550	0·997	1·020	0·977
0·035	0·290	0·984	0·987	0·977	0·18	0·581	1·000	1·031	0·976
0·040	0·304	0·983	0·988	0·974	0·20	0·611	1·001	1·032	0·975
0·050	0·330	0·980	0·989	0·975	0·24	0·666	1·006	1·044	0·975
0·060	0·355	0·985	0·992	0·976					

* The small differences in the densities of solutions of these electrolytes do not cause significant differences in the $I^{\frac{1}{2}}$ values.

1·7, and 1·9 × 10^{-4}, together with a number of theoretical curves calculated from equation (33) with $\mathring{a} = 10$ and the values of b shown. From a comparison of these curves, and of many others not shown, the " best value " of K_{ap} was selected.

Exact agreement with the theoretical curves cannot be expected because they refer to a single electrolyte, while the solutions we are considering contain in addition the products of the solvent self-dissociation. Since the concentration of self-dissociation species decreases with increasing concentration of added electrolyte any deviation from the theoretical curves is expected to be greatest at low concentrations of the added electrolyte and to become negligible at higher concentrations. It seems reasonable to expect that the electrolytes resulting from the dissociation, *i.e.*, H_3O,HSO_4 and H_3SO_4,HS_2O_7, would behave in a similar fashion to the other electrolytes that we have investigated, while the non-electrolytes might be expected, at least in the small concentrations in which they are present, to have little effect on the osmotic coefficient. If it is also assumed that there are no large specific interactions between the various electrolytes and non-electrolytes present, no large deviations from the theoretical osmotic coefficient curves which fit the various electrolytes at higher concentrations would be expected even at lower concentrations. All the experimental curves must, of course, approach the value $\phi = 0{\cdot}98$ at the value of $I^{\frac{1}{2}}$ corresponding to the pure acid.

FIG. 2. *Determination of the value of* K_{ap} *for* $MHSO_4$.



Broken curves are calculated by means of equation (33) *with* $\mathring{a} = 10$ *and the values of* b *indicated on the curves. In each triad of curves* $K_{ap} = 1{\cdot}9$, $1{\cdot}7$, *and* $1{\cdot}5 \times 10^{-5}$ *in descending vertical sequence.*

The osmotic coefficient curves for $K_{ap} = 1{\cdot}9 \times 10^{-4}$ all show a rapid initial rise followed by a much flatter portion which is not consistent with any theoretical curve. This behaviour is further accentuated at higher values of K_{ap} and it seems reasonable to conclude that it arises because the value of K_{ap} is too high. A similar although rather less marked effect is given by the osmotic coefficient curves calculated on the basis of $K_{ap} = 1{\cdot}8 \times 10^{-4}$.

On the other hand, the osmotic coefficients calculated by using $K_{ap} = 1{\cdot}5 \times 10^{-4}$ show a greater and more rapid initial decrease than is consistent with the various theoretical curves which fit the experimental values at higher concentrations. Again, decreasing the value of K_{ap} even further accentuates this effect and it may be concluded that these values of K_{ap} are too low. The intermediate value of $K_{ap} = 1{\cdot}7 \times 10^{-4}$ mole^2 kg.$^{-2}$ seems to give about the most reasonable osmotic coefficient curves in all cases and it was therefore selected as the " best " value. A possible error of $0{\cdot}1 \times 10^{-4}$ seems likely and it does not appear to be possible to determine the value more accurately by the present method.

The Ionic Self-dehydration Constant, K_{id}.—The value of K_{ap} having been determined, the ionic self-dehydration constant K_{id} was determined from the freezing points for solutions of water. Values of the concentrations of all the species in water solutions were calculated for values of $K_{id} = 2{\cdot}5$, $3{\cdot}5$, $4{\cdot}0$, and $5{\cdot}5 \times 10^{-5}$, and $K_{ap} = 1{\cdot}7 \times 10^{-4}$, $K_a = 1{\cdot}4 \times 10^{-2}$, and $K_b = \infty$, *i.e.*, by assuming that water is fully ionised. Other values of K_a were used during the preliminary calculations but, as expected, had little effect on the concentrations of the species as the concentrations of $H_2S_2O_7$ and $HS_2O_7^-$ are both very small in this system. Thus K_{id} could be determined essentially independently of the value of K_a. From the total concentrations of species at different stoicheiometric concentrations of water, and the freezing-point depressions θ calculated from the freezing points given in the previous paper,[4] values of the osmotic coefficient ϕ were calculated by means of equation (28). Table 3 gives the concentrations of all the species and their total concentration Σm_{ij} for rounded concentrations of water. Table 10 gives values of the osmotic coefficients corresponding to the values $K_{id} = 3{\cdot}5 \times 10^{-5}$, $K_{ap} = 1{\cdot}7 \times 10^{-4}$, and $K_a = 1{\cdot}4 \times 10^{-2}$.

TABLE 10. *Osmotic coefficients of water solutions.*

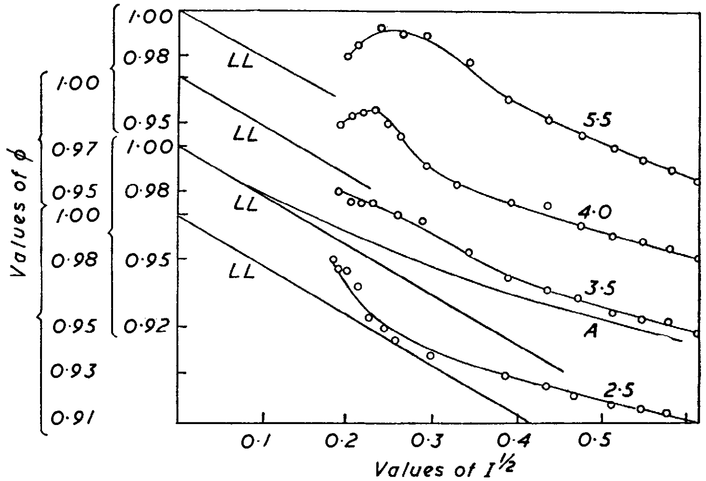
	$K_b = \infty$		$K_b = 1$			$K_b = \infty$		$K_b = 1$	
m^s (H_2O)	$I^{\frac{1}{2}}$	ϕ	$I^{\frac{1}{2}}$	ϕ	m^s (H_2O)	$I^{\frac{1}{2}}$	ϕ	$I^{\frac{1}{2}}$	ϕ
0·000	0·189	0·980	0·189	0·980	0·08	0·389	0·942	0·375	0·977
0·005	0·196	0·984	0·195	0·981	0·10	0·431	0·937	0·413	0·979
0·010	0·204	0·976	0·203	0·976	0·12	0·470	0·933	0·447	0·978
0·015	0·216	0·975	0·214	0·976	0·14	0·506	0·927	0·477	0·982
0·020	0·229	0·975	0·227	0·978	0·16	0·540	0·924	0·505	0·987
0·025	0·243	0·978	0·241	0·979	0·18	0·572	0·921	0·532	0·988
0·03	0·258	0·970	0·255	0·976	0·20	0·602	0·916	0·556	0·992
0·04	0·287	0·967	0·282	0·979	0·24	0·657	0·911	0·600	0·992
0·06	0·341	0·953	0·332	0·979	0·28	0·708	0·906	0·639	0·997

Similar tables were computed for each of the values of K_{id} given above. Fig. 3 shows plots of ϕ against $I^{\frac{1}{2}}$ for each of these values of K_{id}, together with some theoretical curves for comparison. The curve corresponding to $K_{id} = 2{\cdot}5 \times 10^{-5}$ shows very rapid initial decrease and at one point almost coincides with the Debye–Hückel limiting-law curve. With lower values of K_{id} some less complete calculations showed that this effect was accentuated. It was concluded that K_{id} must be greater than $2{\cdot}5 \times 10^{-5}$. On the other hand, for $K_{id} = 4{\cdot}0 \times 10^{-5}$, ϕ initially increases before passing through a maximum value and decreasing at higher concentrations. For higher values of K_{id}, *e.g.*, $5{\cdot}5 \times 10^{-5}$, this behaviour is accentuated, and it was therefore concluded that the value must be less than $4{\cdot}0 \times 10^{-5}$. The curve for $K_{id} = 3{\cdot}5 \times 10^{-5}$ seems to be of reasonable shape and to compare well with the theoretical curves; therefore this was chosen as the best value of K_{id}: it was confirmed by considering the freezing points of oleum solutions.

The Incomplete Dissociation of Water.—The marked decrease in the osmotic coefficients of water with increasing concentration differs from the behaviour of the osmotic coefficients of alkali-metal hydrogen sulphate solutions. It is, in particular, different from that of $KHSO_4$ and NH_4HSO_4, which H_3O,HSO_4 might perhaps be expected to resemble. The most plausible explanation appears to be that the ionisation of water is not quite complete; and, indeed, if a dissociation constant of the order of unity is assumed, an osmotic coefficient curve is obtained which falls between those of $KHSO_4$ and NH_4HSO_4 and agrees well with a theoretical curve. The concentrations of species in water solutions in sulphuric acid, on the assumption that $K_b = 1$, are given in Table 4, and the corresponding osmotic coefficients in Table 10. The incomplete dissociation of water is more fully discussed in the following paper.

The Acid Dissociation Constant, K_a, of Disulphuric Acid.—The values of K_{ap} and K_{id} having been determined it was possible to determine K_a from the freezing points of oleums by essentially the procedure described above. Values of K_a in the range 0·010—0·020 were considered in trial calculations. Table 5 gives the concentrations of all the species in oleum and the osmotic coefficient for $K_{ap} = 1{\cdot}7 \times 10^{-4}$, $K_{id} = 3{\cdot}5 \times 10^{-5}$, and $K_a = 0{\cdot}014$; Fig. 4 illustrates the osmotic coefficient curves obtained for $K_a = 0{\cdot}012$, 0·014, and 0·016. Since disulphuric acid $H_2S_2O_7$ is only a weak electrolyte the change in ionic concentration with its increasing stoicheiometric concentration is small. In fact, because of the repression of the self-dissociation equilibria, the ionic strength of the solution initially decreases very slightly before slowly increasing as the concentration of oleum is further increased. It would be expected therefore that ϕ would change only rather slowly with increasing concentration of oleum, particularly at low concentrations, and would probably show a roughly linear dependence on concentration, as would be expected for a non-electrolyte. Values of K_a equal to, or less than, 0·012 give an osmotic coefficient curve which increases rapidly with increasing molality at low concentrations and then more slowly at higher concentrations. For $K_a = 0{\cdot}016$ the osmotic-coefficient curve shows an initial rapid decrease followed by a minimum and then a slow increase. For higher values of K_a the initial decrease is still faster. Thus it was concluded that the value of 0·016 was too high while 0·012 is too low. The intermediate value of 0·014 gives an almost linear osmotic curve with an initial zero slope, and was chosen as the best value.

Fig. 3. *Determination of the value of K_{id}.*

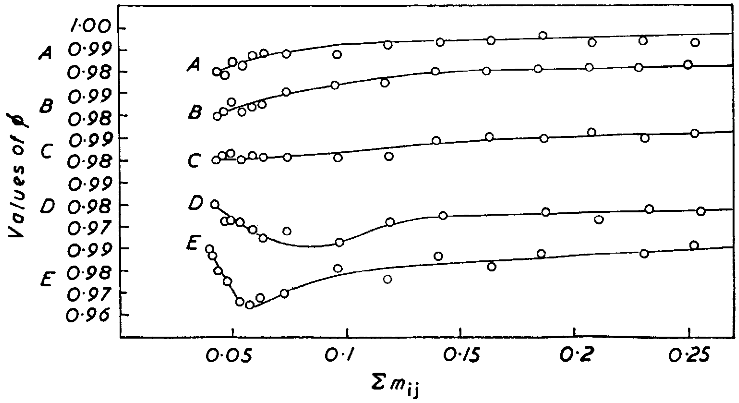


LL = Debye–Hückel limiting law, i.e., equation (32) with å = 2. Numerals on curves are K_{id}.
A, Calc. by means of equation (32) with å = 2.

It should be noted that the value 0·014 applies only to the most dilute oleums, as at higher concentrations oleums contain other polysulphuric acids such as $H_2S_3O_{10}$ and $H_2S_4O_{13}$. These acids are stronger than disulphuric acid and would cause an apparent increase in the dissociation constant K_a calculated on the basis that $H_2S_2O_7$ is the only acid present. It is not possible to separate the effect of small unknown amounts of polysulphuric acids from activity effects, and no detailed interpretation of the osmotic coefficient curve can be given.

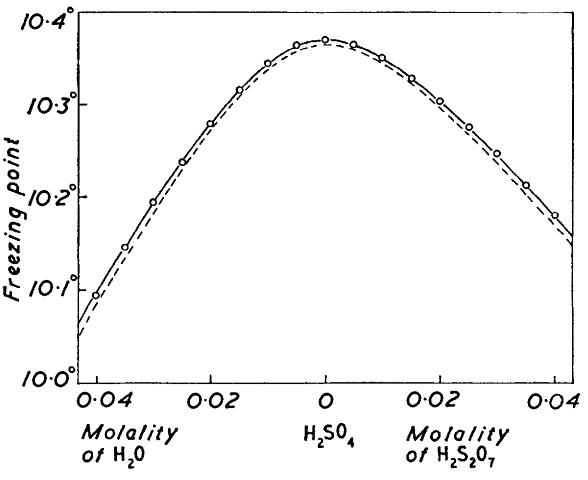
Fig. 4 also shows the effect on ϕ for disulphuric acid solution of varying K_{id}, with $K_{ap} = 1{\cdot}7 \times 10^{-4}$ and $K_a = 0{\cdot}014$. Since a value $2{\cdot}5 \times 10^{-5}$ for K_{id} gives an initial sharp decrease in ϕ while one of $4{\cdot}0 \times 10^{-5}$ gives an initial increase, the value $3{\cdot}5 \times 10^{-5}$ is clearly more satisfactory, as was also concluded above from the freezing points of solutions of water.

FIG. 4. *Determination of the value of K_a.*



Curve	A	B	C	D	E
10^5K_{id}	4·0	3·5	3·5	3·5	2·5
10^5K_a	0·014	0·012	0·014	0·016	0·014

FIG. 5. *Comparison of experimental and calculated freezing points for the* H_2O–SO_3 *system in the region of the composition* H_2SO_4.



—○— *Experimental curve.* - - - - *Calculated curve.*

Fig. 5 shows the experimental freezing points for the H_2O–SO_3 system in the region of the composition H_2SO_4 compared with those calculated by means of equation (28) with $\phi = 1$ and the values of Σm_{ij} given in Tables 4 and 5.

Methods of Correcting for Solvent Dissociation in Solutions of Electrolytes.—For solutes which ionise as simple acids or bases in sulphuric acid, and for substances which ionise by simple dehydration to give rise to oxonium and hydrogen sulphate ions in equal amounts, *e.g.*, $EtOH + 2H_2SO_4 = EtHSO_4 + H_3O^+ + HSO_4^-$, it is simple to correct for unrepressed solvent self-dissociation in any solution, as the concentrations of self-dissociation species may be obtained from Tables 2, 3, and 6.

For complex electrolytes it is, in principle, possible to calculate the concentrations of all the solute species in any solution by the methods outlined above, as shown in the particular case of XOH (Table 7). In practice this is often tedious. It is the purpose of this section to show that it is often not necessary to carry out the complete calculation for each electrolyte. If, as in many cases, we are interested in finding the number of moles of particles, ν, produced in solution by one mole of solute, a simple approximate calculation is adequate. We assume that autoprotolysis is essentially independent of the other self-dissociation equilibria and that therefore the concentration of the autoprotolysis ions ($H_3SO_4^+$ and HSO_4^-) is determined by the amount of added HSO_4^- (or $H_3SO_4^+$), while the concentrations of the other species (H_3O^+, $HS_2O_7^-$, and $H_2S_2O_7$; water is assumed to be fully ionised) are determined by the concentration of added H_3O^+. (Cases where the added electrolyte produces $HS_2O_7^-$ or $H_2S_2O_7$ are of less interest since they are rare, but they could easily be dealt with in a similar manner.) We may then find the concentration of autoprotolysis ions $m_\alpha = m(H_3SO_4^+) + m(HSO_4^-) - m^s(HSO_4^-)$, for any stoicheiometric concentration of HSO_4^- from the values given in Table 2 for strong bases. The concentration of the remaining self-dissociation species [*i.e.*, $m_\beta = m(H_3O^+) + m(HS_2O_7^-) + m(H_2S_2O_7) - m^s(H_3O^+)$] for any stoicheiometric concentration of H_3O^+ may similarly be found from the values for water given in Table 3. Values of m_α and m_β are given in Table 11.

TABLE 11. *Approximate concentrations of self-dissociation species in solutions of electrolytes producing* HSO_4^- *and* H_3O^+.

m^s (HSO_4^-)	m_α	m^s (HSO_4^-)	m_α	m^s (H_3O^+)	m_β	m^s (H_3O^+)	m_β
0·01	0·0191	0·10	0·0036	0·01	0·0081	0·10	0·0008
0·02	0·0142	0·12	0·0028	0·02	0·0047	0·12	0·0006
0·03	0·0110	0·14	0·0023	0·03	0·0030	0·14	0·0006
0·04	0·0088	0·16	0·0017	0·04	0·0020	0·16	0·0004
0·06	0·0063	0·18	0·0012	0·06	0·0014	0·18	0·0004
0·08	0·0045	0·20	0·0010	0·08	0·0009	0·20	0·0003
		0·24	0·0003			0·24	0·0002
		0·28	−0·0001			0·28	0·0000

The accuracy of this approximate method has been tested by comparing values of ν calculated from both the exact and the approximate concentration of self-dissociation species for several types of electrolyte.

From equation (28) we have

$$6{\cdot}12\phi\Sigma m_{ij} = \theta(1 + 0{\cdot}002\theta)$$

Now

$$\Sigma m_{ij} = \nu m^s + m_d$$

Hence

$$\nu = \theta(1 + 0{\cdot}002\theta)/6{\cdot}12\phi m^s - m_d/m^s \quad . \quad . \quad . \quad . \quad . \quad (34)$$

Since in general ϕ is not known it is necessary to set ϕ equal to unity and to calculate an approximate value of ν denoted by ν', where

$$\nu' = \theta(1 + 0{\cdot}002\theta)/6{\cdot}12m^s - m_d/m^s \quad . \quad . \quad . \quad . \quad . \quad (35)$$

If we use the approximate method of obtaining m_d outlined above we may then write:

$$m_d = m_\alpha + m_\beta$$

and

$$\nu'' = \theta(1 + 0{\cdot}002\theta)/6{\cdot}12m^s - (m_\alpha + m_\beta)/m^s \quad . \quad . \quad . \quad . \quad (36)$$

Values of ν' and ν'' are compared for the electrolytes $NaHSO_4$, H_2O, $Ph_3C{\cdot}OH$, and H_3BO_3 in Table 12. In the case of $NaHSO_4$ the total concentration of the species H_3O^+, $HS_2O_7^-$, and $H_2S_2O_7$ remains approximately constant and a mean value of $m_\beta = 0{\cdot}0133$ was taken. In the other cases the appropriate values of m_α and m_β were obtained from Table 11. It may be seen that in all cases agreement between ν' and ν'' is very good, in general better than 1%. This is certainly more than adequate since the assumption that $\phi = 1$ may introduce greater errors.

TABLE 12. *Approximate values of* ν (ν' *and* ν'') *for some electrolytes.*

$NaHSO_4$			$Ph_3C{\cdot}OH$			H_2O			H_3BO_3		
m^s	ν'	ν''	m^s	ν'	ν''	m^s	ν'	ν''	m^s	ν'	ν''
0·04	1·97	1·98	0·02	3·77	3·82	0·04	1·92	1·90	0·015	6·25	6·22
0·06	1·98	1·98	0·03	3·74	3·78	0·06	1·90	1·90	0·02	6·04	6·10
0·08	1·99	1·98	0·04	3·80	3·81	0·08	1·87	1·87	0·03	5·97	5·97
0·10	2·00	2·00	0·05	3·86	3·86	0·10	1·87	1·87	0·04	5·85	5·85
0·12	2·01	2·01	0·06	3·89	3·90	0·12	1·87	1·87	0·05	5·79	5·79
0·14	2·03	2·02	0·07	3·94	3·94	0·14	1·86	1·86	0·06	5·74	5·72
0·16	2·05	2·05	0·08	3·94	3·93	0·16	1·86	1·86	0·07	5·68	5·69
0·18	2·06	2·06	0·09	3·98	3·97	0·18	1·85	1·85	0·08	5·60	5·61
0·20	2·07	2·06	0·10	4·01	4·01	0·20	1·84	1·84			
0·24	2·11	2·11				0·24	1·83	1·83			
0·28	2·11	2·11				0·28	1·81	1·81			

We may note that from equation (34) we obtain:

$$\nu\phi = \theta(1 + 0{\cdot}002\theta)/6{\cdot}12m^s - m_d\phi/m^s$$

Hence $$\nu' \approx \phi\nu$$

It is also important, in calculating the stoicheiometric concentrations (m^s) of a complex electrolyte such as $Ph_3C{\cdot}OH$ or H_3BO_3, to allow for the sulphuric acid consumed in the reaction of the electrolyte with the solvent. This is one reason why equation (35) differs from the equation that has been used to calculate ν in previous Parts of this series [*e.g.*, equation (1) in reference 13]. In this previous equation the molality of the solute (m_2) was the apparent molality calculated without allowance for solvent used in the ionisation of the solute. Allowance was made for this in the equation by the appropriate introduction of s, the number of moles of solvent used in the ionisation of one mole of the solute. Equation (35) also differs from this earlier equation because of the use of the *molal* osmotic coefficient ϕ in the former and the *rational* osmotic coefficient g in the latter. Since, even at the highest concentrations that have generally been used in the measurement of freezing-point depression in sulphuric acid, ϕ differs from g by only 2% (see footnote, p. 827), it is not important for the purpose of determining values of ν whether ϕ or g is set equal to unity. Finally, in the earlier equation, θ represented the freezing-point depression corrected by subtracting an approximate value for the freezing-point depression due to the self-dissociation species while, in equation (35), θ represents the actual freezing-point depression calculated from T_* (10·625°) and allowance for the self-dissociated species is made by means of the term m_d/m^s.

We conclude that the approximate method outlined above for obtaining the concentrations of the self-dissociation species (m_d) is adequate for calculating values of ν in all the cases tested, and it may presumably be used for any electrolyte which ionises to give HSO_4^- and H_3O^+ ions and other ions not common with the solvent. Electrolytes which ionise to give $H_3SO_4^+$ and $HS_2O_7^-$ are much less common but they may be evidently treated in the same manner.

Table 11 thus summarises all the information needed to make adequate allowance for the concentration of self-dissociation species in the calculation of ν for most complex types of electrolyte.

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[*Received, May* 12*th*, 1959.]

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[13] Flowers, Gillespie, and Oubridge, *J.*, 1956, 1925.