843. *Solutions in Sulphuric Acid. Part XXXII.* Molar Conductivities of Some Acids and Bases. Proton-transfer Conduction by the* $H_3SO_4^+$ *and* HSO_4^- *Ions.*

By R. H. Flowers, R. J. Gillespie, E. A. Robinson, and C. Solomons.

Molar conductivities of a number of acids and bases have been calculated from the experimental results of Part XXX.[2] The conductivities of these solutions are due almost exclusively to the ions $H_3SO_4^+$ and HSO_4^- which conduct by a proton-transfer mechanism. By allowing for the small contribution to the conductivity from the other ions, including those resulting from the solvent self-dissociation, molar conductivities of $H_3SO_4^+$ in solutions of acids, and of HSO_4^- in solutions of bases, have been obtained. The molar conductivities of these ions depend on their concentrations and also on the nature and concentration of the accompanying cations: this is discussed in terms of the proton-transfer mechanism for conduction. Activation energies for proton-transfer conduction in sulphuric acid are obtained and are compared with those for proton-transfer conduction in water. The apparent discrepancy between the conclusions drawn from cryoscopic and conductometric measurements with regard to the apparent incomplete dissociation of silver, thallous, and oxonium hydrogen sulphates is discussed.

It has been established [1] that the electrical conductivity of sulphuric acid and of solutions of acids and bases in sulphuric acid is due almost entirely to proton-transfer conduction by the ions $H_3SO_4^+$ and HSO_4^-. Values for the molar conductivities of these ions in various electrolyte solutions are derived in this paper and are discussed in terms of the proton-transfer mechanism of conduction.

Table 1 gives molar conductivities of ammonium, oxonium, and some metal hydrogen sulphates, which all behave as bases, and of disulphuric acid and tetra(hydrogen sulphato)-boric acid, calculated from the experimental results of Part XXX [2] by means of the usual expression $\Lambda = 10^3\kappa/c$, where c is the molar concentration of the electrolyte. These molar conductivities approach infinity at infinite dilution (see curve *B*, Fig. 1) because of the finite conductivity of the solvent. The conductivity of the solvent cannot be allowed for simply by subtracting it from the conductivity of the solution because the self-ionisation of the solvent that is responsible for this conductivity is repressed by the added electrolyte. It is necessary to make use of the self-dissociation constants given in the preceding paper [3] to calculate the extent of solvent self-dissociation. The results of these calculations for solutions of acids and bases at 25° are given in Tables 2—5. Molal concentrations were converted into molar concentrations by using the densities given in Part XXIX.[4]

The Molar Conductivity of the HSO_4^- *Ion in Solutions of Strong Bases.*—The specific conductance of a solution of a strong base $X(HSO_4)_n$, ionising according to the equation

$$X(HSO_4)_n \rightleftharpoons X^{n+} + nHSO_4^-$$

is given by

$$\kappa = 10^{-3}(c_{H_3SO_4^+}\lambda_{H_3SO_4^+} + c_{HSO_4^-}\lambda_{HSO_4^-} + c_{H_3O^+}\lambda_{H_3O^+} + c_{HS_2O_7^-}\lambda_{HS_2O_7^-} + c_{X^{n+}}\lambda_{X^{n+}} \quad . \quad (1)$$

The transport numbers of univalent metal ions fall in the range 0·02—0·03 and do not vary appreciably with concentration over the range with which we are concerned.[5] Since the

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* Part XXXI, preceding paper.

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

[2] Bass, Flowers, Gillespie, Robinson, and Solomons, *J.*, 1960, 4315.

[3] Part XXXI, Gillespie, Robinson, and Solomons, preceding paper.

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

[5] Gillespie and Wasif, *J.*, 1953, 209.

molar conductivities of univalent metal sulphates $MHSO_4$ vary from approximately 150 at $c = 0{\cdot}01$ to approximately 80 at $c = 0{\cdot}5$ (Table 7), we conclude that $\lambda_{M^+} = 3$—5 over this composition range. For simplicity we will in fact assume, for all univalent ions ($X^{\pm}$), excepting $H_3SO_4^+$ and HSO_4^-, but including in particular H_3O^+ and $HS_2O_7^-$, and for all concentrations in the range with which we are concerned, that $\lambda_{X^{\pm}} = 5$. This

TABLE 1. *Molar conductances, Λ, for solutions of metal hydrogen sulphates at 25°.*

	$10^3\Lambda$										
c	$LiHSO_4$	$NaHSO_4$	$KHSO_4$	$RbHSO_4$	$CsHSO_4$	NH_4HSO_4	$AgHSO_4$	$TlHSO_4$	$H_3O{\cdot}HSO_4$	$H_2S_2O_7$	$HB(HSO_4)_4$
0·01	1·0500	1·0500	1·0520	—	—	1·0530	1·0530	—	1·0460	1·0540	1·0510
0·02	0·5340	0·5340	0·5370	0·5400	0·5400	0·5380	0·5380	0·5400	0·5305	0·5340	0·5365
0·03	0·3677	0·3677	0·3700	0·3733	0·3733	0·3710	0·3700	0·3733	0·3633	0·3630	0·3700
0·04	0·2863	0·2868	0·2890	0·2925	0·2913	0·2903	0·2888	0·2925	0·2825	0·2785	0·2908
0·06	0·2086	0·2100	0·2123	0·2150	0·2142	0·2130	0·2108	0·2150	0·2082	0·1948	0·2143
0·08	0·1723	0·1736	0·1760	0·1800	0·1800	0·1774	0·1744	0·1800	0·1735	0·1531	0·1800
0·10	0·1520	0·1536	0·1558	0·1610	0·1610	0·1590	0·1545	0·1605	0·1530	0·1281	0·1611
0·15	0·1253	0·1266	0·1293	0·1340	0·1347	0·1327	0·1280	0·1360	0·1273	0·0949	0·1359
0·20	0·1115	0·1130	0·1162	0·1200	0·1205	0·1188	0·1145	0·1225	0·1142	0·0777	0·1196
0·25	0·1022	0·1040	0·1076	0·1112	0·1114	0·1098	0·1060	0·1134	0·1056	0·0671	0·1140
0·30	0·0952	0·0973	0·1012	0·1047	0·1050	0·1037	0·0998	0·1063	0·0998	0·0596	0·1040
0·35	0·0899	0·0919	0·0963	0·0994	0·1006	0·0987	0·0950	0·1007	0·0947	0·0541	0·0960
0·40	0·0848	0·0873	0·0919	0·0943	0·0965	0·0946	0·0905	0·0966	0·0900	0·0498	0·0900
0·45	0·0803	0·0833	0·0880	0·0901	0·0928	0·0910	0·0873	0·0929	0·0864	0·0463	0·0842
0·50	0·0770	0·0795	0·0845	0·0880	0·0894	0·0878	0·0830	0·0896	0·0830	0·0434	0·0792
0·60	0·0705	0·0728	0·0787	0·0807	0·0833	0·0823	0·0770	0·0835	0·0772	0·0388	0·0705
0·70	0·0651	0·0684	0·0737	0·0764	0·0787	0·0777	0·0724	0·0789	0·0724	0·0353	0·0617
0·80	0·0605	0·0652	0·0696	—	—	—	0·0684	—	0·0680	—	—

	$10^3\Lambda$				$10^3\Lambda$		
c	$Ca(HSO_4)_2$	$Sr(HSO_4)_2$	$Ba(HSO_4)_2$	c	$Ca(HSO_4)_2$	$Sr(HSO_4)_2$	$Ba(HSO_4)_2$
0·02	0·5700	0·5700	0·5775	0·12	0·1991	0·1996	0·2108
0·03	0·4150	0·4150	0·4267	0·14	0·1914	0·1900	0·1993
0·04	0·3413	0·3413	0·3525	0·16	0·1831	0·1816	0·1931
0·05	0·2990	0·2970	0·3090	0·18	0·1722	0·1678	0·1789
0·06	0·2717	0·2692	0·2817	0·20	0·1615	0·1600	0·1708
0·07	0·2514	0·2493	0·2636	0·24	0·1467	0·1467	0·1569
0·08	0·2369	0·2344	0·2463	0·28	0·1364	0·1357	0·1452
0·09	0·2244	0·2222	0·2361	0·32	0·1269	0·1261	0·1350
0·10	0·2145	0·2125	0·2265				

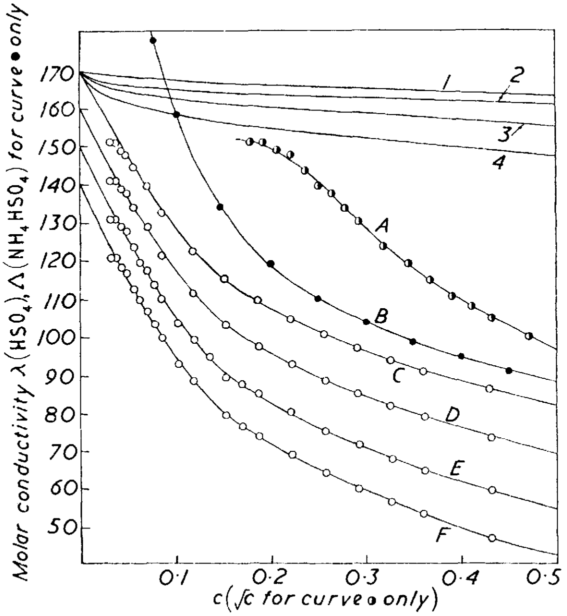

FIG. 1. *Molar conductivities of metal hydrogen sulphates.*

Eqn. (8): curve 1, ε = 100, $\mathring{a} = 10$; curve 2, ε = 80, $\mathring{a} = 10$; curve 3, ε = 100, $\mathring{a} = 2$; curve 4, ε = 80 $\mathring{a} = 2$.

A, *B*, *C*, NH_4; *D*, K; *E*, Na; *F*, Li.

Curves C, D, E, and F are successively displaced vertically by —10 *units.*

is probably an upper limit and for some ions and some concentrations $\lambda_{X^\pm}$ may well be smaller than this. However, since $\lambda_{X^\pm}$ is very much smaller than $\lambda_{HSO_4^-}$ even a 100% error in any of the $\lambda_{X^\pm}$ values would not cause an error of more than a few units % in $\lambda_{HSO_4^-}$. The transport numbers of bivalent metal ions M^{2+} have been found[5] to be of the order 0·01, and therefore we assume $\lambda_{M^{2+}} = 1{\cdot}5$.

TABLE 2. *Molal concentrations of species for the strong acid–sulphuric acid system at 25°.*

m	$m_{H_3SO_4^+}$	$m_{HSO_4^-}$	$m_{H_3O^+}$	$m_{HS_2O_7^-}$	$m_{H_2S_2O_7}$	m_{A^-}
0·000	0·0135	0·0178	0·0088	0·0045	0·0043	0·0000
0·010	0·0180	0·0133	0·0096	0·0042	0·0054	0·0100
0·020	0·0237	0·0101	0·0103	0·0039	0·0064	0·0200
0·040	0·0376	0·0064	0·0121	0·0033	0·0088	0·0400
0·060	0·0535	0·0045	0·0139	0·0029	0·0110	0·0600
0·120	0·1060	0·0023	0·0185	0·0022	0·0163	0·1200
0·180	0·1609	0·0015	0·0224	0·0018	0·0206	0·1800
0·240	0·2170	0·0011	0·0257	0·0016	0·0241	0·2400
0·360	0·3305	0·0007	0·0314	0·0012	0·0302	0·3600

TABLE 3. *Molal concentrations of species for the strong base–sulphuric acid system at 25°.*

m	$m_{H_3SO_4^+}$	$m_{HSO_4^-}$	$m_{H_3O^+}$	$m_{HS_2O_7^-}$	$m_{H_2S_2O_7}$	m_{M^+}
0·000	0·0135	0·0178	0·0088	0·0045	0·0043	0·0000
0·010	0·0102	0·0237	0·0083	0·0048	0·0035	0·0100
0·020	0·0078	0·0308	0·0080	0·0050	0·0030	0·0200
0·040	0·0051	0·0471	0·0074	0·0054	0·0020	0·0400
0·060	0·0037	0·0653	0·0072	0·0056	0·0016	0·0600
0·120	0·0019	0·1229	0·0068	0·0058	0·0010	0·1200
0·180	0·0013	0·1819	0·0066	0·0060	0·0006	0·1800
0·240	0·0010	0·2413	0·0065	0·0062	0·0003	0·2400
0·360	0·0007	0·3608	0·0064	0·0063	0·0001	0·3600

TABLE 4. *Molal concentrations of species for the disulphuric acid–sulphuric acid system at 25°.*

m	$m_{H_3SO_4^+}$	$m_{HSO_4^-}$	$m_{H_3O^+}$	$m_{HS_2O_7^-}$	$m_{H_2S_2O_7}$
0·000	0·0135	0·0178	0·0088	0·0045	0·0043
0·010	0·0163	0·0147	0·0056	0·0072	0·0084
0·020	0·0189	0·0127	0·0040	0·0102	0·0138
0·040	0·0236	0·0102	0·0023	0·0157	0·0265
0·060	0·0277	0·0087	0·0019	0·0209	0·0412
0·120	0·0378	0·0064	0·0012	0·0326	0·0885
0·180	0·0462	0·0050	0·0009	0·0421	0·1387
0·240	0·0536	0·0045	0·0007	0·0498	0·1907
0·360	0·0661	0·0036	0·0006	0·0631	0·2978

TABLE 5. *Molal concentrations of species for the water–sulphuric acid system at 25° (water is assumed to be fully ionised).*

m	$m_{H_3SO_4^+}$	$m_{HSO_4^-}$	$m_{H_3O^+}$	$m_{HS_2O_7^-}$	$m_{H_2S_2O_7}$
0·000	0·0135	0·0178	0·0088	0·0045	0·0043
0·010	0·0106	0·0226	0·0147	0·0027	0·0020
0·020	0·0082	0·0291	0·0227	0·0018	0·0010
0·040	0·0053	0·0456	0·0412	0·0009	0·0003
0·060	0·0038	0·0640	0·0609	0·0007	0·0002
0·120	0·0019	0·1223	0·1204	0·0003	0·0001
0·180	0·0014	0·1814	0·1802	0·0002	0·0000
0·240	0·0010	0·2410	0·2402	0·0002	0·0000
0·360	0·0007	0·3607	0·3601	0·0001	0·0000

We may now calculate a " corrected conductivity " for any base

$$\begin{aligned}\kappa' &= \kappa - (c_{H_3O^+}\lambda_{H_3O^+} + c_{HS_2O_7^-}\lambda_{HS_2O_7^-} + c_{X^{n+}}\lambda_{X^{n+}}) \\ &= c_{HSO_4^-}\lambda_{HSO_4^-} + c_{H_3SO_4^+}\lambda_{H_3SO_4^+} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (2)\end{aligned}$$

It has been shown in the preceding paper[3] that, independently of concentration, $\lambda_{H_3SO_4^+}/\lambda_{HSO_4^-} = 1{\cdot}45$. Hence

$$\kappa' = \lambda_{-}(1{\cdot}45c_{H_3SO_4^+} + c_{HSO_4^-}) \quad . \; . \; . \; . \; . \; . \quad (3)$$

where $\lambda_{-} = \lambda_{HSO_4^-}$. Table 6 gives values of κ' calculated from equation (2) by using the experimental κ values given in Part XXX[2] and the concentrations of species given in Tables 3 and 5. The values of λ_{-} given in Table 7 were calculated by means of equation

(4) from these values of κ' and the concentrations of $H_3SO_4^+$ and HSO_4^- given in Tables 3 and 5.

Fig. 1 shows values of λ_- for NH_4HSO_4, $KHSO_4$, $NaHSO_4$, and $LiHSO_4$ plotted against $c_{HSO_4^-}$, and for NH_4HSO_4 plotted against $\sqrt{c_{HSO_4^-}}$. The plots against $c_{HSO_4^-}$ appear to be approximately linear at concentrations below 0·1 and can be extrapolated to $c_{HSO_4^-} = 0$, giving a value of $\lambda_-^0 = 170$ in each case. Similar plots were made for all the other hydrogen sulphates investigated and they were all very similar to those shown and extrapolated to the same value of λ_-^0 in each case. The more conventional plot of λ against $\sqrt{c_{HSO_4^-}}$ appears to be S-shaped and is difficult to extrapolate. The lowest concentration than is accessible in sulphuric acid, $c_{HSO_4^-} = 0·0178$, is, in fact, already higher that the concentration at which the plot of λ_- against $\sqrt{c}$ might be expected to be linear.

TABLE 6 *Conductivities* ($\kappa' \times 10^2$) *corrected for the contribution due to ions other than* $H_3SO_4^+$ *and* HSO_4^-.

m	$LiHSO_4$	$NaHSO_4$	$KHSO_4$	$RbHSO_4$	$CsHSO_4$	NH_4HSO_4	$AgHSO_4$	$TlHSO_4$
0·000	1·032	1·032	1·032	1·032	1·032	1·032	1·032	1·032
0·005	1·034	1·034	1·034	—	—	1·034	1·034	—
0·010	1·046	1·048	1·049	—	—	1·049	1·048	—
0·015	1·067	1·071	1·075	—	—	1·075	1·074	—
0·020	1·098	1·103	1·109	—	—	1·112	1·107	—
0·030	1·185	1·190	1·201	1·221	1·221	1·208	1·196	1·221
0·040	1·289	1·292	1·309	1·343	1·343	1·318	1·301	1·343
0·060	1·516	1·534	1·560	1·604	1·606	1·569	1·542	1·614
0·080	1·755	1·779	1·817	1·879	1·901	1·844	1·797	1·926
0·100	2·000	2·027	2·075	2·159	2·189	2·114	2·056	2·223
0·120	2·236	2·266	2·331	2·426	2·471	2·371	2·301	2·506
0·140	2·458	2·487	2·573	2·683	2·738	2·623	2·533	2·773
0·160	2·655	2·700	2·800	2·925	2·995	2·860	2·760	3·035
0·180	2·847	2·897	3·017	3·167	3·247	3·087	2·952	3·287
0·200	2·999	3·079	3·224	3·394	3·489	3·304	3·169	3·539
0·240	3·328	3·443	3·608	3·848	3·938	3·723	3·548	3·998
0·280	3·607	3·732	3·952	4·217	4·362	4·097	3·922	4·437
0·320	3·846	3·986	4·266	4·581	4·746	—	4·156	4·851
0·360	—	4·224	—	4·965	5·135	—	—	5·225
0·400	—	—	—	5·195	5·405	—	—	5·495

m	$H_3O{\cdot}HSO_4$ $K_b = \infty$	$H_3O{\cdot}HSO_4$ $K_b = 1$	$H_2S_2O_7$	$HB(HSO_4)_4$	*m*	$Ca(HSO_4)_2$	$Sr(HSO_4)_2$	$Ba(HSO_4)_2$
0·000	1·032	1·032	1·032	1·032	0·00	1·032	1·032	1·032
0·005	1·032	1·032	1·040	1·038	0·01	1·122	1·122	1·122
0·010	1·043	1·043	1·054	1·046	0·02	1·337	1·337	1·359
0·015	1·066	1·066	1·072	1·076	0·03	1·571	1·554	1·610
0·020	1·096	1·096	1·092	1·115	0·04	1·805	1·784	1·858
0·030	1·180	1·180	1·139	1·210	0·05	2·042	2·014	2·108
0·040	1·291	1·291	1·188	1·325	0·06	2·284	2·234	2·354
0·060	1·546	1·546	1·287	1·596	0·07	2·508	2·448	2·598
0·080	1·808	1·808	1·383	1·882	0·08	2·696	2·641	2·806
0·100	2·072	2·072	1·475	2·18	0·09	2·880	2·825	3·005
0·120	2·320	2·320	1·562	2·45	0·10	3·053	2·993	3·193
0·140	2·560	2·561	1·643	2·67	0·12	3·360	3·290	3·525
0·160	2·792	2·793	1·719	2·86	0·14	3·547	3·487	3·742
0·180	3·012	3·013	1·791	3·11	0·16	3·834	3·774	4·054
0·200	3·224	3·226	1·859	3·14	0·18	4·036	3·981	4·281
0·240	3·606	3·608	1·988	3·37	0·20	4·218	4·168	4·478
0·280	3·958	3·968	2·102	3·57				
0·320	4·274	4·296	2·208	3·72				
0·360	4·568	4·604	2·303	3·84				
0·400	4·838	4·885	2·369	3·91				

The Molar Conductivity of the $H_3SO_4^+$ *Ion in Solutions of Acids.*—For an acid HA ionising according to the equation

$$HA + H_2SO_4 = H_3SO_4^+ + A^- \quad . \; . \; . \; . \; . \; . \; . \quad (4)$$

we have $\kappa' = \kappa - (c_{H_3O^+}\lambda_{H_3O^+} + c_{HS_2O_7^-}\lambda_{HS_2O_7^-} + c_{A^-}\lambda_{A^-})$

$$= c_{H_3SO_4^+}\lambda_{H_3SO_4^+} + c_{HSO_4^-}\lambda_{HSO_4^-} \quad . \quad . \quad . \quad . \quad . \quad (5)$$

and since $\lambda_{H_3SO_4^+}/\lambda_{HSO_4^-} = 1{\cdot}45$

we have $\kappa' = \lambda_+(c_{H_3SO_4^+} + c_{HSO_4^-}/1{\cdot}45) \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$

where $\lambda_+ = \lambda_{H_3SO_4^+}$

Table 6 gives values of κ' calculated from equation (5) by using the experimental κ values given in Part XXX [2] for $H_2S_2O_7$ and $HB(HSO_4)_4$ and the concentrations of species given in Tables 2 and 4, it being assumed that $HB(HSO_4)_4$ is a strong acid. Values of λ_+ were then calculated by means of equation (6). These values are given in Table 8 and are plotted against $c_{H_3SO_4^+}$ in Fig. 2. These plots are linear at low concentrations, like those of $\lambda_{HSO_4^-}$ against $c_{HSO_4^-}$, and can be extrapolated to $c_{H_3SO_4^+} = 0$, giving $\lambda_+^0 = 245$ for $HB(HSO_4)_4$ and $\lambda_+^0 = 232$ for $H_2S_2O_7$. We can also obtain a value for λ_+^0 from the relation $\lambda_+^0 = 1{\cdot}45\lambda_-^0 = 247$ which is in very good agreement with the value obtained from the $HB(HSO_4)_4$ results. The lower value obtained from the $H_2S_2O_7$ results is probably due to the fact that higher polysulphuric acids are present to an increasing extent with increasing concentration. Since these higher polysulphuric acids seem to be stronger acids than disulphuric acid,[6] the $H_3SO_4^+$ concentration is probably greater than that calculated from the dissociation constant $K_a = 0{\cdot}014$ for disulphuric acid. Hence the apparent λ_+ values would be expected to be increasingly greater, as $c_{H_2S_2O_7}$ increases, than the true values, and consequently the plot of λ_+ against $c_{H_3SO_4^+}$ might have

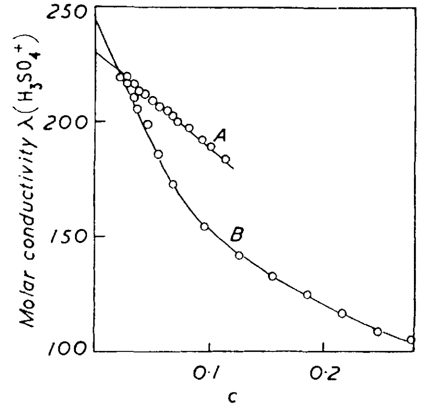

FIG. 2. *Molar conductivities of* (*A*) $H_2S_2O_7$ *and* (*B*) $HB(HSO_4)_4$

TABLE 7. *Values for the mobility of the* HSO_4^- *ion* (λ_-) *in solutions of hydrogen sulphates.*

	λ_-									
m	Li	Na	K	Rb	Cs	NH_4	Ag	Tl	H_2O $K_b = \infty$	H_2O $K_b = 1$
0·000	151·2	151·2	151·2	151·2	151·2	151·2	151·2	151·2	151·2	151·2
0·010	148·5	149·0	149·0	—	—	149·0	149·6	—	149·8	149·9
0·020	143·0	143·6	144·0	—	—	144·8	144·2	—	146·5	147·3
0·040	129·9	130·2	131·7	135·5	135·5	132·8	131·1	135·5	131·7	136·6
0·060	118·3	119·4	121·5	125·3	125·5	122·3	120·4	125·9	121·8	125·1
0·120	98·5	99·8	102·7	106·9	109·2	104·6	101·3	110·7	101·7	110·4
0·180	86·2	87·7	91·4	96·1	98·9	93·7	89·4	99·7	90·2	101·6
0·240	76·7	79·3	83·2	89·0	91·5	86·1	81·7	92·5	81·7	94·2
0·360	—	65·9	—	78·0	77·4	—	—	82·2	69·5	—

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

a smaller slope than expected and would extrapolate to give a low value of λ_+^0. Thus we assume that $\lambda_+^0 = 245$ is the better value but it is difficult to give any estimate of the probable error.

TABLE 8. *Values for the mobility of the* $H_3SO_4^+$ *ion* (λ_+) *in solutions of acids.*

m	$H_2S_2O_7$ *	$HB(HSO_4)_4$ †	*m*	$H_2S_2O_7$ *	$HB(HSO_4)_4$ †	*m*	$H_2S_2O_7$ *	$HB(HSO_4)_4$ †
0·000	219·2	219·2	0·04	212·4	172·7	0·18	197·6	105·1
0·010	218·9	210·5	0·06	209·5	154·2	0·24	191·9	82·1
0·020	215·8	198·8	0·12	202·0	124·6	0·36	183·7	63·5

* $K_a = 0·014$. † Assuming $K_a = \infty$.

Comparison of λ_- *Values with the Robinson and Stokes Conductance Equation.*—For the relatively high concentrations with which we are concerned in sulphuric acid it is necessary, for comparison with our experimental results, to use a modified form of the Debye–Hückel–Onsager equation such as that proposed by Robinson and Stokes.[7] This equation makes use of Falkenhagen, Leist, and Kelbg's calculation [8] of the effect of the finite size of ions on the conductivity, but it differs slightly from the equation proposed by Falkenhagen *et al.* themselves, as these authors based their equation on a distribution function due to Wicke and Eigen,[9] while Robinson and Stokes's equation is based on the usual Boltzmann distribution function. For our purposes the difference is negligible and we shall use the slightly simpler equation of Robinson and Stokes which, for a 1 : 1 electrolyte, is as follows:

$$\Lambda = \left(\Lambda_0 - \frac{B_2\sqrt{c}}{1 + B\mathring{a}\sqrt{c}}\right)\cdot\left(1 - \frac{B_1\sqrt{c}}{1 - B\mathring{a}\sqrt{c}}\cdot\frac{e^{0·2929B\mathring{a}\sqrt{c}} - 1}{0·2929B\mathring{a}\sqrt{c}}\right) \quad . \quad . \quad (7)$$

where Λ is the molar conductivity at concentration *c*, Λ_0 is that at infinite dilution, $B = 50·29(\varepsilon T)^{-1/2}$, $B_1 = 8·204 \times 10^5(\varepsilon T)^{-3/2}$, $B_2 = 82·5/[\eta(\varepsilon T)^{1/2}]$, $\mathring{a}$ is the mean diameter of anion and cation, ε is the dielectric constant, and *T* is the absolute temperature. The term in the first parentheses gives the diminution in the molar conductivity due to the electrophoretic effect, and that in the second parentheses is due to the relaxation effect. Substituting $\varepsilon = 100$,[10] $T = 298°$ K, $\eta = 24·54$,[11] and $\mathring{a} = 10$, and assuming that $\lambda_{HSO_4^-} = \Lambda_{MHSO_4}$ we may write for the hydrogen sulphate ion

$$\lambda_{HSO_4^-} = \left(\lambda^0{}_{HSO_4^-} - \frac{1·948\sqrt{c}}{1 + 1·2900\sqrt{c}}\right)\cdot\left(1 - \frac{0·1572\sqrt{c}}{1 + 2·900\sqrt{c}}\cdot\frac{e^{0·8493\sqrt{c}} - 1}{0·8493\sqrt{c}}\right) \quad (8)$$

The conductivity curve for the hydrogen sulphate ion calculated by means of this equation is shown in Fig. 1. It may be seen that it predicts a very much smaller decrease in the equivalent conductivity with increasing concentration than that actually observed. The value of $\mathring{a} = 10$ was obtained previously from cryoscopic measurements on solutions of the same electrolytes.[12] However, even if a much smaller value, such as $\mathring{a} = 2$, is used the change in the predicted conductivity curve is relatively slight and no agreement with the experimental curves can be obtained with any positive value of $\mathring{a}$. It is just possible that the dielectric constant could be in error [10] but the value cannot be less than that for water, and even if we take $\varepsilon = 80$, and $\mathring{a} = 2$, there is still a very large discrepancy between the predicted and the observed curves. It is uncertain whether or not a correction should be made for the change in the viscosity of the solutions, or how such a correction should

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[7] Robinson and Stokes, "Electrolyte Solutions," Butterworths, 1955, p. 151.

[8] Falkenhagen, Leist, and Kelbg, *Ann. Phys.*, 1952, **51**, 11.

[9] Wicke and Eigen, *Z. Elektrochem.*, 1952, **56**, 551; 1953, **57**, 319.

[10] Gillespie and Cole, *Trans. Faraday Soc.*, 1956, **52**, 1325; Gillespie and White, *Trans. Faraday Soc.*, 1958, **54**, 1846.

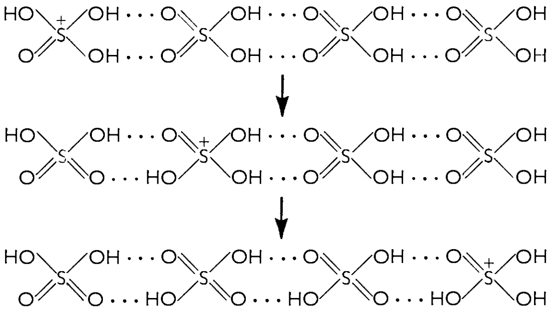
[11] Gillespie and Wasif, *J.*, 1953, 215.

[12] Bass, Gillespie, and Oubridge, *J.*, 1960, 837.

be made,[11,13] but even if the conductivity is multiplied by the relative viscosity [14] the effect is in general quite small and in no case can it account for more than a small part of the observed difference between the predicted and the observed conductivity curves. The conductivity of aqueous hydrogen chloride solutions is mainly due to proton-transfer conduction by the hydronium ion,[14] and a similar although somewhat smaller discrepancy between the values predicted by equation (7) and observed conductivities has also been found for such solutions at concentrations above $c = 0{\cdot}1$, although this equation accurately predicts the conductivities of several metal chlorides up to high concentrations.[14]

Proton-transfer Conduction in Sulphuric Acid.—It is evident therefore that equation (7) does not hold for proton-transfer conduction. The mechanism of this process consists of (*a*) the orientation of solvent molecules around the conducting ions and the formation of suitable hydrogen bonds along which proton transfer can occur, and (*b*) the transfer of protons along these hydrogen bonds—in sulphuric acid from a sulphuric acid molecule to a hydrogen sulphate ion or from a sulphuric acidium ion to a sulphuric acid molecule. There now seems to be reasonably good evidence [15] that (*a*) is the rate-determining step of this process in liquid water, and it is probable that this will also be the case in sulphuric acid. The proton-transfer process for the $H_3SO_4^+$ ion in sulphuric acid can be represented diagrammatically as in (*A*) which shows a succession of proton transfers along a hydrogen-bonded chain of suitably oriented sulphuric acid molecules. After successive proton transfers have occurred along this chain, the molecules are left with a different orientation and no further proton transfers can take place in the same direction until the sulphuric acid molecules again have a suitable orientation.

(*A*)



It has been suggested by Onsager [16] that for aqueous solutions the effect of other ions on the conductivity of the hydronium ion can be attributed to the fact that some of the water molecules will have fixed orientations around ions and will not therefore have the freedom of rotation necessary for them to take part in proton-transfer conduction. Since it has been shown [4,12] that ions in sulphuric acid are solvated just as they are hydrated in water, the decrease in the conductivity of the hydrogen sulphate ion with increasing electrolyte concentration may be similarly explained as being caused by the " tying-up " of solvent molecules in the solvation shells of ions. These molecules are presumably unable, or at least less able, to participate in the proton-transfer. Thus a hydrogen sulphate ion will less frequently encounter a suitably oriented sulphuric acid molecule and the conductivity of the hydrogen sulphate ion will be correspondingly decreased.

This explanation also accounts for the specific effects of different cations which will depend on the extent of their solvation. Table 9 lists all the cations, the conductivities

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[13] Stokes, " The Structure of Electrolyte Solutions," Edited by Hamer, Wiley, 1959, p. 298.

[14] Ref. 7, pp. 153, 362.

[15] Eigen and de Maeyer, " The Structure of Electrolytic Solutions," ed. Hamer, Wiley, New York, 1959, p. 64.

[16] Onsager, *Ann. New York Acad. Sci.*, 1945, **46**, 265.

of whose hydrogen sulphates have been measured, in order of decreasing molar conductivity and therefore presumably of increasing extent of solvation. Solvation numbers of the cations deduced from freezing-point [12] and density measurements [4,11] are also given. It may be seen that the order of decreasing solvation of the cations given by these two methods agrees closely with that suggested by conductivity measurements, and this provides strong support for the above explanation of the decrease in molar conductivity of the hydrogen sulphate ion with increasing concentration and the specific effects of different cations.

TABLE 9. *Comparison of the relative extent of cation solvation as deduced from conductivity measurements with solvation numbers obtained from cryoscopic and density measurements.*

	$\lambda_{HSO_4^-}$ at	Solvation numbers			$\lambda_{HSO_4^-}$ at	Solvation numbers	
Cation	$c_{M^+} = 0{\cdot}2$	Cryoscopy	Density	Cation	$c_{M^+} = 0{\cdot}2$	Cryoscopy	Density
Tl	97·5	—	0	Ag	86·9	2·1	1·5
Cs	96·3	—	0	Na	84·4	3·0	3
Rb	93·4	—	1	Li	82·3	2·3	2
NH_4	90·9	1·2	1	Ba	63·2	6·5	5
K	88·5	2·1	2	Ca	59·2	—	8
H_3O	87·2 (98·5 *)	1·8	0·3	Sr	58·6	—	8

* Assuming $K_b = 1$.

However, the differences between the different metal hydrogen sulphates are relatively small, while there is a large difference between all the observed curves and that predicted by equation (8). This appears to imply that all the cations are extensively but slightly differently solvated. If this is so, the solvation must be of a different kind from that measured in the freezing-point [12] and density measurements.[4,11] The latter apparently measure only primary solvation, and the solvation numbers refer just to those molecules held tightly in the first solvation layer, while conductivities give a measure of primary plus secondary solvation which extends less strongly over a number of solvent layers around the ion. If we make the simple assumption that the conductivity is proportional to the concentration of " free " sulphuric acid molecules, *i.e.*, molecules that are *not* part of the solvation layers, so that

$$\lambda = \lambda_{\text{eqn. (8)}} \frac{\text{concentration of `` free '' } H_2SO_4}{\text{total concentration of } H_2SO_4} \quad . \quad . \quad . \quad (9)$$

then solvation numbers of the order of 35—40 are needed to account for the observed conductivity at $c = 0{\cdot}1$, decreasing to 10—12 at $c = 1$. However, part of the conductivity decrease can be attributed to the fact that *any* solute must, to some extent at least, occupy sites in the liquid that would be otherwise occupied by sulphuric acid molecules, so that when a hydrogen sulphate ion arrives at an adjacent site, no proton is available for it to accept and thus the proton-transfer process is hindered and the mobility of the hydrogen sulphate ion correspondingly decreased. Even the hydrogen sulphate ion itself will behave in this way since when two hydrogen sulphate ions arrive on adjacent sites no proton transfer can occur. We may write

$$\lambda = \lambda_{\text{eqn. (8)}} p/p^0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

where p represents the average probability, in a solution of a base, that a hydrogen sulphate ion can acquire a proton from an adjacent sulphuric acid molecule, and p^0 the average probability in the pure solvent. For large solute molecules p would be expected to decrease with increasing molecular size and this is probably the main reason for the observed differences in the conductivities of various ketones.[2] It does not seem possible at present to make even a semiquantitative calculation of this probability factor, which will include the solvation effect discussed above, but it is evident that its value will decrease with increasing concentration of the electrolyte, or of any other electrolyte or non-electrolyte.

We have no direct evidence that, apart from this probability factor, the conductivity would be given by equation (8), but Robinson and Stokes have argued [17] that it should be, and this equation does appear to hold for aqueous hydrogen chloride solutions at concentrations up to $c = 0{\cdot}1$. The molecularly equivalent concentration in sulphuric acid is $c = 0{\cdot}03$, and as the concentration of HSO_4^- in H_2SO_4 itself is 0·018, because of the solvent self-dissociation, it is not possible to test directly the applicability of equation (8) to sulphuric acid solutions. Because of the high dielectric constant and high viscosity of sulphuric acid, the effect of the factors considered in equation (8) is in any case considerably less than the effect of the probability factor discussed above.

Comparison of Proton-transfer Conductivities in Sulphuric Acid and Water.—Values of the molar conductivities of $H_3SO_4^+$ and HSO_4^- are summarised in Table 10, which gives both the values extrapolated to infinite dilution (λ^0) and the values for 100% H_2SO_4 (λ^{100}). The extrapolated values may be regarded as somewhat uncertain in view of the lack of any theoretical justification for the extrapolation. The molar conductivities (λ^0) are predominately due to proton-transfer conduction (λ^0_p) but they do contain a small contribution due to normal diffusion conduction (λ^0_n), *i.e.*, $\lambda^0 = \lambda^0_p + \lambda^0_n$. The contribution of the normal diffusion mechanism to the molar conductivity (λ^0_n) is very probably of the same order of magnitude as that for other ions, *i.e.*, $\lambda^0_n \sim 5$. This is comparable with the possible error in the molar conductivities and we will not therefore correct for it but will assume that the experimental values given in Table 10 are entirely due to proton-transfer conduction.

TABLE 10. *Proton-transfer mobilities in water and sulphuric acid at 25°.*

	H_2SO_4			H_2O		
	λ^0	λ^{100}		λ^0	λ^0_n	λ^0_p
HSO_4^-	170	150	OH^-	200	76·4,[a] 55·4[b]	124—145
$H_3SO_4^+$ ...	245	220	H_3O^+	350	90,[c] 73·5,[d] 38·6[e]	260—311

[a] $\lambda^0_{Cl^-}$. [b] $\lambda^0_{F^-}$. [c] Calc. from the self-diffusion coefficient for water. [d] $\lambda^0_{K^+}$. [e] $\lambda^0_{Li^+}$.

It is interesting to compare these values with the limiting molar conductivities of the H_3O^+ and OH^- ions in water, which are also given in Table 10. These values contain a substantial contribution from the normal or diffusion mechanism of conduction which is much more important in water than in sulphuric acid because of the much smaller viscosity of water. It is difficult to make an accurate allowance for the normal contribution to the conductivity. In the case of H_3O^+ it has been common practice [18] to assume that the normal mobility is the same as that of Na^+ ($\lambda^0 = 50{\cdot}1$) but there seems to be little real justification for this. The radius of the H_3O^+ ion is approximately 1·4 Å which is more nearly equal to that of K^+ or NH_4^+ for both of which $\lambda^0 = 73{\cdot}5$. On the other hand, there is good evidence [15,19] that H_3O^+ is solvated by three water molecules while both K^+ and NH_4^+ are solvated by less than one water molecule,[19] and the solvated ions would therefore be much smaller than the solvated H_3O^+. From this point of view comparison with Li^+ ($\lambda^0 = 38{\cdot}7$), for which a solvation number of 3·4 has been suggested,[19] would be more reasonable. This is supported by the fact that several properties of the H_3O^+ ion in aqueous solution are closely similar to those of Li^+.[15] Robinson and Stokes [20] have suggested that the normal diffusion mobility of the H_3O^+ ion should be approximately the same as the diffusion mobility of a water molecule in liquid water which may be calculated from the self-diffusion coefficient. This leads to the value $\lambda^0_n = 90$. Thus

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[17] Ref. 7, p. 360.

[18] Hückel, *Z. Elektrochem.*, 1928, **34**, 540.

[19] Glueckauf, *Trans. Faraday Soc.*, 1955, **51**, 1235.

[20] Ref. 7, p. 116.

although a value of 300 is often given for $\lambda^0_p(H_3O^+)$, a number of values in the range 260—311 seem equally probable. In the case of OH^- the normal contribution to the conductivity has often been assumed to be equal to that of Cl^- ($\lambda^0 = 76{\cdot}4$) but it was suggested by Wannier [21] that it is more likely to be about the same as that of F^- ($\lambda^0 = 55{\cdot}4$) which is much more nearly the same size as OH^-. However, this ignores the possibility of differences in the extents of solvation of OH^- and F^-. We can conclude that proton-transfer molar conductivities are of the same order of magnitude in both sulphuric acid and water but in neither solvent are they known very accurately.

Because the hydrogen bonds in sulphuric acid are probably stronger and shorter than those in water it is reasonable to assume that proton transfer along such hydrogen bonds will be at least as fast as in water. Thus it is probable that in sulphuric acid, as in water, the rate-determining step of the proton-transfer conduction is the orientation of solvent molecules and the formation of hydrogen bonds. This process is evidently hardly affected by the high viscosity of sulphuric acid and it cannot therefore involve the same amount of hydrogen-bond breaking and formation as in the viscous flow of sulphuric acid.

It is noteworthy that HSO_4^- has a smaller proton-transfer mobility than $H_3SO_4^+$ in H_2SO_4 just as OH^- has a smaller proton-transfer mobility than H_3O^+ in water. On the assumption that proton transfer is the rate-determining step of proton-transfer conduction, Gierer and Wirtz [22] explained the difference in the conductivities of H_3O^+ and OH^- in water as being due to the fact that proton transfer for H_3O^+ occurs between essentially neutral oxygen atoms while for OH^- it occurs between negatively charged oxygen atoms and the latter process would be expected to have a higher activation energy. Similar considerations would be expected to apply to conduction by $H_3SO_4^+$ and HSO_4^- in H_2SO_4. The ratio $(\lambda^0_+)_p/(\lambda^0_-)_p$ is 2·2 for water but only 1·45 for sulphuric acid. This difference could be plausibly accounted for on the grounds that the charge on HSO_4^- is more dispersed than in OH^- and thus the charges on the oxygen atoms between which the proton moves are smaller for HSO_4^- than OH^-. It is probable, however, that proton-transfer is not the rate-determining step and thus the differences in the mobilities of the lyonium and lyate ions in the two solvents must probably be explained in another way. Presumably, the orientation of a solvent molecule in the immediate vicinity of a lyonium or a lyate ion and subsequent hydrogen-bond formation is faster for the lyonium ion than for the lyate ion. From simple electrostatic considerations this seems plausible, but it does not seem possible to make any quantitative calculations until we have considerably more knowledge of the structure of these solutions.

Activation Energies for Proton-transfer Conduction.—Apparent activation energies, E, for the proton-transfer conduction process can be obtained from the expression

$$\lambda = Ae^{-E/RT} \qquad (11)$$

where λ is the molar conductivity of either the lyonium or lyate ion and A is a non-exponential factor. By using values of the temperature coefficients α_+ and α_- obtained from Table 4 of the preceding paper,[3] apparent activation energies for the temperature ranges 10—25° and 25—40° were calculated from equation (11) and are given in Table 11. Since it has been shown [3] that $\alpha_+ = \alpha_-$, it follows that $E_+ = E_-$. It is interesting to compare these values with the activation energies for the proton-transfer

TABLE 11. *Arrhenius parameters for proton-transfer conduction.*

		E (kcal./mole)		$10^{-5}A$				E (kcal./mole)		$10^{-5}A$	
		10—25°	25—40°	10—25°	25—40°			10—25°	25—40°	10—25°	25—40°
H_2SO_4	$H_3SO_4^+$	4·5	4·2	4·0	2·5	H_2O	H_3O^+	2·5	2·3	0·21	0·16
	HSO_4^-	4·5	4·2	2·8	1·7		OH^-	3·5	2·8	0·22	0·26

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[21] Wannier, *Ann. Physik*, 1935, **24**, 545.

[22] Gierer and Wirtz, *Ann. Physik*, 1949, **6**, 257.

conduction of H_3O^+ and OH^- in water. These were calculated from the appropriate molar conductivities on the assumption that

$$(\lambda^0{}_p)_{H_3O^+} = \lambda^0{}_{H_3O^+} - \lambda^0{}_{Li^+}$$
$$(\lambda^0{}_p)_{OH^-} = \lambda^0{}_{OH^-} - \lambda^0{}_{F^-}$$

and are also given in Table 11. It may be seen that the apparent activation energies are greater for $H_3SO_4^+$ and HSO_4^- in sulphuric acid than for H_3O^+ and OH^- in water. Since the actual values of the molar conductivities are of the same order of magnitude in sulphuric acid and water, it follows that the non-exponential factor A must be greater in sulphuric acid than in water. These values of A are also given in Table 11.

The values given in Table 11 have been called apparent activation energies because they probably do not refer to a single process; however, it seems likely that the most important activated process is the reorientation of solvent molecules in the neighbourhood of an ion and the associated formation and breaking of hydrogen bonds. This will be more difficult and therefore have a higher activation energy in sulphuric acid than in water because of the greater number and strength of hydrogen bonds in sulphuric acid than in water. Because of the extensive and strong hydrogen-bonding in liquid sulphuric acid, it is likely that there are extensive regions of more or less ordered structure through which protons are rapidly transferred, and only occasionally at some defect in the structure is it necessary for any reorientation of solvent molecules and hydrogen-bond formation to occur. This is consistent with the non-exponential A factor's being relatively large for proton-transfer conduction in sulphuric acid.

For both H_2SO_4 and H_2O the activation energies for proton-transfer conduction decrease with increasing temperature which may be attributed to easier reorientation of solvent molecules as the solvent structure is broken up by increasing thermal motion. Breaking-up of the solvent structure will hinder the proton-transfer process, and the value of A decreases correspondingly, but the decrease in the activation energy is more important and the proton-transfer conductivities increase with increasing temperature. It has been shown by Gierer and Wirtz [22] that for water at a sufficiently high temperature the conductivities of H_3O^+ and OH^- pass through a maximum and thereafter decrease with increase in temperature, presumably because the breaking-up of the solvent structure has then become the most important factor in determining the rate of proton-transfer conduction.

The Incomplete Dissociation of Silver, Thallous, and Oxonium Hydrogen Sulphates.—It has been concluded from cryoscopic measurements [12,23] that silver, thallous, and oxonium hydrogen sulphates are incompletely dissociated. This conclusion was based on the observation that these electrolytes have osmotic coefficients which are less than unity and decrease with increasing concentration up to the highest concentrations investigated, whereas all the other electrolytes that have been investigated have osmotic coefficients which, after decreasing to a minimum, increase with increasing concentration to values greater than unity. Osmotic coefficients greater than unity can be easily accounted for in terms of solvation of the cations, while the anomalously low osmotic coefficients could be attributed to " negative-solvation," *i.e.*, breaking-up of the solvent structure by the cation, or to incomplete dissociation. Now although the large thallium ion, which density measurements [4] indicate is not solvated, may be a structure-breaking ion, this is unlikely to be the case for the smaller Ag^+ and H_3O^+ ions which density measurements [4] show to be solvated (Table 9). Thus for these two ions at least incomplete dissociation seems to be the only explanation of the anomalously low osmotic coefficients of their solutions.

No indication of incomplete dissociation, however, appears in the conductivities of solutions of the hydrogen sulphates of H_3O^+, Ag^+, and Tl^+ which when plotted against c

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

give curves of the same form as those of fully dissociated electrolytes. If we allow for incomplete dissociation of H_3O,HSO_4, using $K_b = 1$ to calculate the molar conductivity of the hydrogen sulphate ion in solutions of water, we obtain values which seem unreasonably large, being greater than those for any of the metal hydrogen sulphates (Table 7). We must conclude therefore either that the freezing points must be explained in some other way than in terms of incomplete dissociation or that this incomplete dissociation does not affect the conductivity of the solution. In order to obtain further information which might shed more light on this problem some further experiments were carried out. Conductivities of solutions containing mixtures of potassium and oxonium hydrogen sulphates were measured, and the results of one such experiment are shown in Table 12. The conductivities of the mixtures are almost identical with the conductivity of the same concentrations of potassium hydrogen sulphate alone, although in these solutions it may be shown that if $K_b = 1$ the water would only be about 85% dissociated and a correspondingly low conductivity would be expected. Experiments with mixtures of silver and potassium hydrogen sulphates similarly gave no indication of any incomplete dissociation of the silver hydrogen sulphate (Table 12).

TABLE 12.

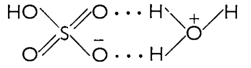
(a) *Conductivities of mixtures of water and potassium hydrogen sulphate in sulphuric acid.*

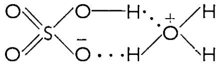
c_{H_2O}	c_{KHSO_4}	c_{total}	$10^2\kappa_{obs.}$	$10^2\kappa_{KHSO_4}$
0·0000	0·3160	0·3160	3·149	3·149
0·0037	0·3156	0·3193	3·172	3·172
0·0102	0·3151	0·3253	3·212	3·212
0·0219	0·3138	0·3357	3·281	3·279
0·0404	0·3123	0·3527	3·390	3·388
0·0624	0·3103	0·3727	3·518	3·510
0·0919	0·3076	0·3995	3·680	3·674
0·1217	0·3049	0·4266	3·842	3·830
0·1835	0·2995	0·4830	4·164	4·145

(a) *Conductivities of mixtures of silver and potassium hydrogen sulphates in sulphuric acid.*

C_{AgHSO_4}	C_{KHSO_4}	C_{total}	$10^2\kappa_{obs.}$	$10^2\kappa_{KHSO_4}$
0·0000	0·1575	0·1575	1·999	1·999
0·0064	0·1575	0·1639	2·048	2·049
0·0183	0·1575	0·1758	2·137	2·137
0·0310	0·1575	0·1885	2·230	2·230
0·0420	0·1575	0·1996	2·312	2·312
0·0595	0·1575	0·2170	2·440	2·440
0·0867	0·1575	0·2442	2·640	2·640

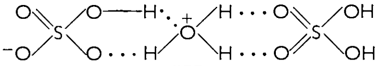
(I)



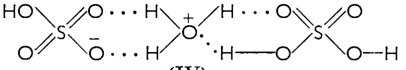


(II)

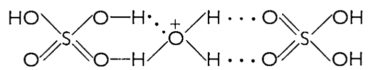
It seems likely therefore that water is completely ionised to oxonium hydrogen sulphate ($H_3O^+ HSO_4^-$) but that it is incompletely dissociated and this incomplete dissociation does not affect the conductivity of the solutions. Presumably the incomplete dissociation results from the formation of a rather strongly hydrogen-bonded ion-pair for which either of the structures (I) and (II) seems plausible. Since it is likely that all the hydrogen atoms and lone pairs on the H_3O^+ will be involved in hydrogen bonding, it seems probable that this ion pair will be solvated by at least one sulphuric acid molecule. Plausible structures for a mono-solvated ion pair are (III) and (IV). Such a solvated ion-pair is closely related to the solvated oxonium-ion complex for which evidence has been obtained from cryoscopic measurements,[12] heat capacities,[24] and Raman spectra.[25] Cryoscopy suggests that the formula is $H_3O(H_2SO_4)_2^+$. The structure (V), related to those above for the oxonium hydrogen sulphate ion-pair, seems plausible.



(III)



(IV)



(V)

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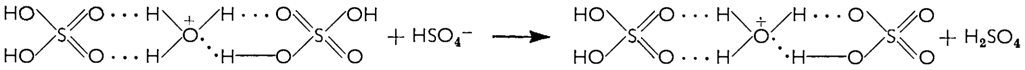
[24] Wyatt, *Trans. Faraday Soc.*, 1960, **56**, 490.

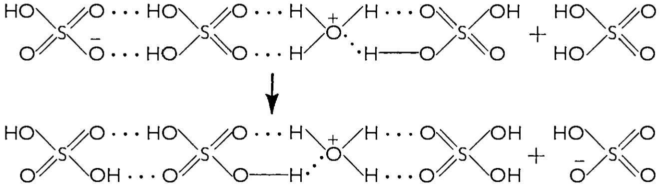
[25] Young and Walrafen, personal communication.

It is possible to account for the unexpectedly high conductivities of solutions containing this ion-pair in two ways. If the life-time of an undissociated ion-pair is appreciably longer than the time of a single molecular vibration, it will be detected in the measurement of any colligative property of the solution if it is present in sufficient concentration. However, if the life-time is nevertheless of the same order of magnitude as the average time for a proton transfer in the conduction process, then the formation of such a relatively short-lived ion-pair will have only a negligible effect on the conductivity. Since ion-pair formation can be written as a proton-transfer as follows



it is reasonable to suppose that the frequency of such a process is of the same order of magnitude as proton-transfer between HSO_4^- and H_2SO_4.

It is also possible that the oxonium ion, unlike other cations, does not reduce the mobility of the hydrogen sulphate ion. The following process in which the sulphuric acid molecules solvating an H_3O^+ ion take part in proton-transfer can be imagined:



Thus, if there is any diminution in conductivity due to the existence of ion-pairs H_3O^+ HSO_4^- this may be offset by a very small, or even negligible, effect of H_3O^+ on the conductivity of HSO_4^-.

In the case of $AgHSO_4$ such a special proton-transfer mechanism is not possible and it is necessary to assume that the life-time of an ion-pair is of the same order of magnitude as, or smaller than, the average time for proton transfer in order to account for the unexpectedly high conductivity and the low osmotic coefficients of silver hydrogen sulphate solutions. For thallous hydrogen sulphate solutions it is possible that the low osmotic coefficient is due to the structure-breaking effect of the large non-solvated Tl^+ ion and that there is no ion-pair formation. If there is ion-pair formation, however, we must again assume that the average life-time of the ion-pairs is comparable to, or less than, the average time of proton transfer.

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