46. *Solutions in Sulphuric Acid. Part XII.* Electrical Conductivity Measurements.*

By R. J. Gillespie and S. Wasif.

The conductivities of solutions in sulphuric acid of ammonium, lithium, sodium, potassium, strontium, and barium hydrogen sulphate, and acetic acid, benzoic acid, acetone, *n*-propylamine, aniline, methyl and ethyl alcohols, nitric acid, triphenylmethanol, *o*-phenylenediamine, dinitrogen tetroxide, hexamethylenetetramine, *p*-nitrotoluene, dichloroacetic acid, sulphuryl chloride, and trichloroacetic acid have been measured.

The effects of the nature of the cation and of concentration on the conductivity of the hydrogen sulphate ion are discussed. The equivalent conductivity of this ion in sulphuric acid is compared with those of the hydrogen and hydroxide ions in water, and the conclusion is drawn that in sulphuric acid molecular rotation is the rate-determining stage of chain conduction, whereas in water proton-transfer is rate-determining.

On the basis of the results of the conductivity measurements, the solutes have been classified as strong, weak, or non-electrolytes, and the strong electrolytes have been further classified according to the number of hydrogen sulphate ions produced by one molecule of electrolyte. The use of conductivity measurements in determining the nature and extent of ionisation of a solute is discussed and compared with the corresponding use of cryoscopic measurements. The effect of non-electrolytes on the conductivity of sulphuric acid is discussed.

THERE has been very little previous work on conductivity measurements in sulphuric acid except that concerned with the solutes water and sulphur trioxide which has been discussed in Part IX (*J.*, 1953, 204). Hantzsch (*Z. physikal. Chem.*, 1907, **61**, 257) investigated the conductivities in sulphuric acid of a wide variety of solutes including the alkali-metal hydrogen sulphates, ammonium hydrogen sulphate, and water, which he showed had reasonably constant and similar equivalent conductivities, and he took the values of the equivalent conductivities of these solutes to be characteristic of a binary electrolyte. Although the equivalent conductivities of the alkali-metal hydrogen sulphates were all similar there were small but definite differences between them, which indicated that the equivalent conductivity increased with increasing molecular weight of the cation, which Hantzsch attributed to an increase in the mobility of the cation with increasing molecular weight. Certain organic compounds which he considered from the results of cryoscopic measurements to behave as binary electrolytes also gave equivalent conductivities similar to, although generally slightly smaller than, those of the alkali hydrogen sulphates. Hantzsch took this as confirmation of their behaviour as binary electrolytes. He concluded also that dichloroacetic acid behaves as a weak acid and that oxalic acid, trichloroacetic acid, trinitro-

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* Part XI, preceding paper.

phenol, phthalic anhydride, and dimethyl sulphate behave as non-electrolytes. Bergius (*ibid.*, 1910, **72**, 338) later carried out very similar work, and attempted to investigate more dilute solutions than Hantzsch had done. He found somewhat different equivalent conductivity values and disputed Hantzsch's claim that the equivalent conductivity was independent of concentration. The general qualitative conclusions of both Hantzsch and Bergius were largely correct, the differences between their results arising mainly from their lack of understanding of the self-dissociation of the sulphuric acid and its repression by added electrolytes; thus they both always incorrectly subtracted the conductivity of the solvent from that of the solution before calculating the equivalent conductivity of the solute.

Usanovitch and his co-workers (*Physikal. Z. Sovietunion*, 1933, **4**, 134; *J. Gen. Chem. U.S.S.R.*, 1935, **5**, 701, 709; 1946, **16**, 1987) studied the conductivities and viscosities of a number of binary systems involving sulphuric acid and an organic compound, *e.g.*, nitrobenzene, trichloroacetic acid, and ether, and claimed that their results showed the existence of various addition compounds *e.g.*, $2M,H_2SO_4$, M,H_2SO_4, $M,2H_2SO_4$ ($M =$ nitrobenzene). Recently Reinhardt (*J. Amer. Chem. Soc.*, 1950, **72**, 3359) has reported a few measurements on the conductivity of potassium hydrogen sulphate in dilute oleums: his results will be discussed in Part XIII.

In the present work the conductivities of solutions of a wide variety of solutes have been studied over a large concentration range. Many of these solutes have previously been investigated cryoscopically (cf. Parts I—VII and references contained therein), and their modes and degree of ionisation established.

EXPERIMENTAL

Apparatus and Experimental Procedure.—The conductivity apparatus has been described in Part IX (*loc. cit.*). Sulphuric acid was prepared in the conductivity cell by adding weighed amounts of water to a weighed amount of dilute oleum until the minimum conductivity was obtained. Successive weighed portions of the solute were then added, and the conductivity measured each time as described in Part IX.

Preparation and Purification of Materials.—The purification of ammonium sulphate and the alkali and alkaline-earth metal sulphates that were used was described in Part X (*J.*, 1953, 209). Methyl alcohol was dried and purified by fractionation through an efficient column. A middle fraction, b. p. 65·0°, was collected.

Ethyl alcohol. To the alcohol (1 l.) ethyl succinate (25 g.) and sodium (8 g.) were added, the mixture refluxed for 4 hours, the alcohol fractionated, and a fraction, b. p. 78·2°, collected (Smith, *J.*, 1927, 1288).

Triphenylmethanol was recrystallised several times from carbon tetrachloride; it had m. p. 162°. *n*-Propylamine was redistilled three times through an efficient column, and a fraction of b. p. 47·5° finally collected. Aniline, twice distilled from zinc dust, had b. p. 180°. *o*-Phenylenediamine was dissolved in hot water containing sodium dithionite (hydrosulphite) and charcoal, filtered, and allowed to crystallise. The colourless crystals obtained were washed with ice-cold water and dried in a vacuum-desiccator; m. p. 100—101°. Hexamethylenetetr-

TABLE 1. *Specific conductivities of some alkali and alkaline-earth metal hydrogen sulphates at 25°.*

Ammonium hydrogen sulphate.

M, mol. l.$^{-1}$	100κ	M, mol. l.$^{-1}$	100κ
0·0268	1·085	0·3214	3·269
0·0417	1·150	0·6152	5·000
0·0600	1·300	1·0384	6·776
0·0825	1·450	1·2984	7·603
0·1066	1·680	1·4836	8·114
0·1199	1·758	1·6660	8·602
0·1381	1·960	1·9002	9·061
0·1773	2·300	1·9990	9·226

Sodium hydrogen sulphate.

M, mol. l.$^{-1}$	100κ	M, mol. l.$^{-1}$	100κ
0·1318	1·736	1·4946	6·468
0·3206	2·997	1·8502	6·828
0·6972	4·711	2·2900	7·042
0·9666	5·505		

Potassium hydrogen sulphate.

M, mol. l.$^{-1}$	100κ	M, mol. l.$^{-1}$	100κ
0·0568	1·256	0·1981	2·315
0·1251	1·740	0·2532	2·170
0·3602	3·380	1·0278	6·360
0·4934	4·156	1·1568	6·695
0·6242	4·783	1·3336	7·112
0·8686	5·834	1·4074	7·224
		1·6148	7·593

Lithium hydrogen sulphate.

M, mol. l.$^{-1}$	100κ	M, mol. l.$^{-1}$	100κ
0·1342	1·760	1·0438	5·334
0·3794	3·277	1·2792	5·683
0·6112	4·247	1·5406	5·957
0·8248	4·876	1·7292	6·087

Strontium hydrogen sulphate.

M, mol. l.$^{-1}$	100κ	M, mol. l.$^{-1}$	100κ
0·0842	1·923	0·5765	4·882
0·1705	2·851	0·6750	5·086
0·2853	3·824	0·8069	5·095
0·3844	4·360	0·9290	5·028
0·4666	4·650		

Barium hydrogen sulphate.

M, mol. l.$^{-1}$	100κ	M, mol. l.$^{-1}$	100κ
0·0688	1·733	0·2599	3·658
0·1371	2·580	0·2988	3·941
0·3865	4·360	0·8448	5·247
0·4760	4·693	0·9513	5·260
0·6096	5·016	1·042	5·234
0·6640	5·152	1·122	5·193
0·7147	5·160	1·200	5·135

TABLE 2. *Specific conductivities of some strong electrolytes at 25°.*

Acetic acid.

M, mol. l.$^{-1}$	100κ	M, mol. l.$^{-1}$	100κ
0·1105	1·622	0·6174	4·700
0·2877	2·908	0·7760	5·328
0·4473	3·872	0·9548	5·908

Benzoic acid.

M, mol. l.$^{-1}$	100κ	M, mol. l.$^{-1}$	100κ
0·1078	1·568	0·6731	4·535
0·2592	2·639	0·7770	4·825
0·3815	3·352	0·9310	5·140
0·5188	3·994		

Acetone.

M, mol. l.$^{-1}$	100κ	M, mol. l.$^{-1}$	100κ
0·0220	1·064	0·4953	4·288
0·0781	1·351	0·6837	5·259
0·1128	1·748	0·7515	5·980
0·1901	2·223	1·0480	6·500
0·3713	3·527		

Nitric acid.

M, mol. l.$^{-1}$	100κ	M, mol. l.$^{-1}$	100κ
0·0080	1·052	0·0850	2·065
0·0148	1·091	0·1040	2·353
0·0219	1·158	0·1115	2·450
0·0292	1·237	0·2192	3·756
0·0402	1·381	0·3452	5·089
0·0524	1·563	0·5100	6·303
0·0615	1·706	0·6525	7·105

n-*Propylamine.*

M, mol. l.$^{-1}$	100κ	M, mol. l.$^{-1}$	100κ
0·1000	1·547	0·6850	5·140
0·2169	2·432	0·8206	5·724
0·3518	3·377	0·9554	6·162
0·4338	3·933	1·0750	6·513
0·5688	4·598		

Aniline.

M, mol. l.$^{-1}$	100κ	M, mol. l.$^{-1}$	100κ
0·0693	1·354	0·7103	5·076
0·2365	2·640	0·8266	5·456
0·3437	3·356	0·9607	5·813
0·4680	4·055	1·0670	6·033
0·5851	4·599		

*Methyl alcohol.**

M, mol. l.$^{-1}$	100κ	M, mol. l.$^{-1}$	100κ
0·0954	1·519	0·8069	5·562
0·2564	2·735	0·9455	6·047
0·4374	3·869	1·104	6·533
0·6008	4·705	1·296	7·020

*Ethyl alcohol.**

M, mol. l.$^{-1}$	100κ	M, mol. l.$^{-1}$	100κ
0·0150	1·044	0·5175	4·380
0·0394	1·124	0·7016	5·216
0·0817	1·408	0·8220	5·657
0·2138	2·467	1·001	6·222
0·3043	3·132		

Triphenylcarbinol.

M, mol. l.$^{-1}$	100κ	M, mol. l.$^{-1}$	100κ
0·0130	1·081	0·0425	1·353
0·0205	1·145	0·0873	2·128
0·0327	1·291		

o-*Phenylenediamine.*

M, mol. l.$^{-1}$	100κ	M, mol. l.$^{-1}$	100κ
0·0474	1·480	0·3413	4·890
0·0737	1·880	0·4452	5·408
0·0954	2·230	0·5526	5·820
0·1000	2·371	0·6767	6·116
0·2037	3·690		

*Dinitrogen tetroxide.**

M, mol. l.$^{-1}$	100κ	M, mol. l.$^{-1}$	100κ
0·0027	1·042	0·0379	1·619
0·0072	1·070	0·0463	1·808
0·0143	1·157	0·0598	2·111
0·0210	1·265	0·0934	2·819
0·0292	1·431	0·1216	3·379

*Hexamethylenetetramine.**

M, mol. l.$^{-1}$	100κ	M, mol. l.$^{-1}$	100κ
0·0089	1·146	0·0520	2·332
0·0221	1·473	0·0743	2·902
0·0325	1·758	0·0969	3·430

* The molarities of these solutes were calculated from the weight concentrations on the assumption that the densities of their solutions are the same as that of sulphuric acid.

TABLE 3. *Specific conductivities of some weak electrolytes at 25°.*

p-*Nitrotoluene.*

M, mol. l.$^{-1}$	100 κ	M, mol. l.$^{-1}$	100 κ
0·0911	1·304	0·5581	2·523
0·2421	1·841	0·6345	2·626
0·3205	2·069	0·7558	2·742
0·3984	2·247	0·9018	2·849
0·4816	2·406		

*Dichloroacetic acid.**

M, mol. l.$^{-1}$	100 κ	M, mol. l.$^{-1}$	100 κ
0·1109	1·166	0·4938	1·665
0·2421	1·355	0·6359	1·835
0·3593	1·512	0·7865	1·964

Disulphuric acid.†

M, mol. l.$^{-1}$	100 κ	M, mol. l.$^{-1}$	100 κ
0·0248	1·056	0·7870	2·554
0·1870	1·493	1·039	2·826
0·3918	1·950	1·291	3·040
0·6011	2·303		

* See footnote to Table 2. † Taken from the results given in Table 1 of Part IX.

TABLE 4. *Specific conductivities of some non-electrolytes at 25°.*

Sulphuryl chloride.

M, mol. l.$^{-1}$			M, mol. l.$^{-1}$		
Solute	H_2SO_4	100κ	Solute	H_2SO_4	100κ
0·0000	18·62	1·033	0·4292	17·89	0·966
0·1212	18·42	1·016	0·5237	17·72	0·951
0·2005	18·28	1·002	0·6711	17·47	0·929
0·2853	18·10	0·989	0·7935	17·23	0·911

*Trichloroacetic acid.**

M, mol. l.$^{-1}$			M, mol. l.$^{-1}$		
Solute	H_2SO_4	100κ	Solute	H_2SO_4	100κ
0·0000	18·62	1·033	0·3502	18·03	0·983
0·1272	18·41	1·016	0·4741	17·84	0·970
0·2451	18·22	0·999	0·5549	17·70	0·961

* See footnote to Table 2.

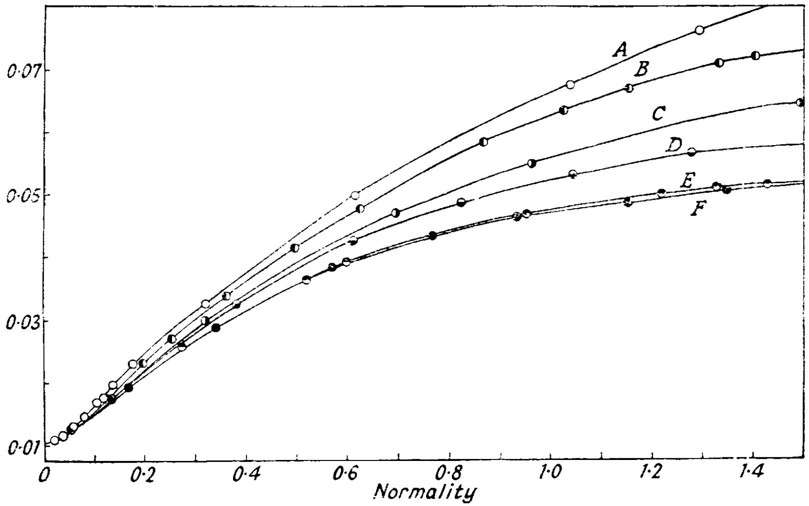
amine was twice recrystallised from alcohol. Acetic acid was distilled from 100% sulphuric acid at room temperature. Benzoic acid was twice recrystallised from hot water and dried in a vacuum-desiccator; m. p. 121°. Dichloroacetic acid was distilled at 26 mm., and the fraction of b. p. 105—107° collected. Trichloroacetic acid was distilled, and the fraction of b. p. 194—196° collected.

Acetone. " AnalaR " material was dried (K_2CO_3) and then distilled through an efficient column, the fraction of b. p. 56·5—57·0° being collected.

Nitric acid was prepared by the method described, *e.g.*, by Hughes, Ingold, and Reed (*J.*, 1950, 2400). Dinitrogen tetroxide was prepared by the method described in Part III (*J.*, 1950, 2504). Sulphuryl chloride was distilled several times, finally through an efficient column, the fraction of b. p. 69·1° being collected.

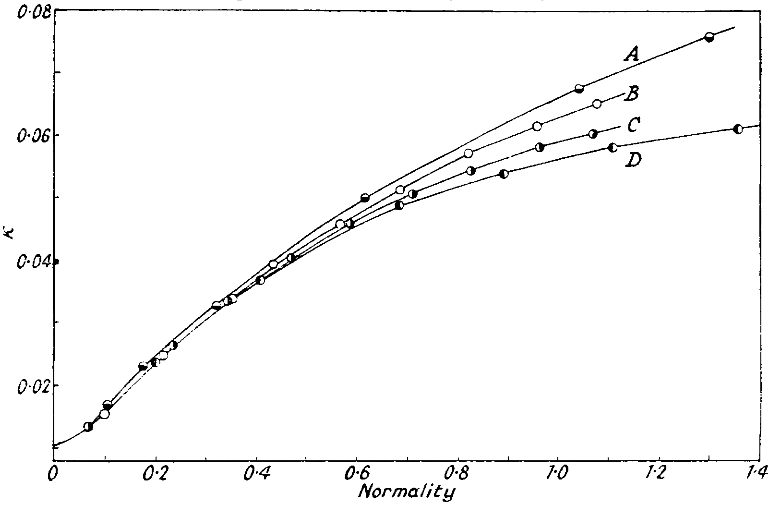
Results.—The specific conductivities, κ, at 25° of all the electrolytes investigated are listed in Tables 1—4, and a selection of them are plotted against concentration in Figs. 1—5. The molarities, M, given in the tables have been calculated from the weight concentrations by utilising density values interpolated from curves based on the data recorded in Part XI. For a few solutes for which the density measurements were not made it was assumed that the densities of their solutions were the same as that of pure sulphuric acid.

FIG. 1. *Specific conductivities of some alkali and alkaline-earth metal hydrogen sulphates.*



A, NH_4HSO_4.
B, $KHSO_4$.
C, $NaHSO_4$.
D, $LiHSO_4$.
E, $Ba(HSO_4)_2$.
F, $Sr(HSO_4)_2$.

FIG. 2. *Specific conductivities of some organic solutes.*



A, NH_4HSO_4. *B*, $NH_2Pr^n{}_2$. *C*, NH_2Ph. *D*, o-$C_6H_4(NH_2)_2$.

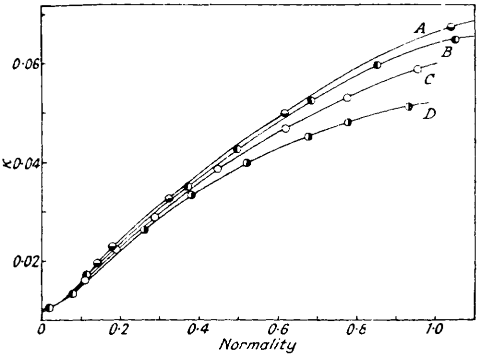
The equivalent and molar conductivities listed in Tables 5 and 6 were calculated from specific-conductivity values taken from plots of specific conductivity against concentration such as are shown in Figs. 1—3. Values of the equivalent and molar conductivity are not listed for solutions containing a total added hydrogen sulphate ion concentration of less than 0·1N since for smaller concentrations the repression of the autoprotolysis of the solvent is substantially incomplete and a correction should be made for this in calculating the equivalent or molar conductivity. For higher concentrations of added hydrogen sulphate ion the conductivity due to the autoprotolytic ions may be ignored without serious error (Part XIII, to follow).

DISCUSSION

The Conductivity of Some Alkali and Alkaline-earth Metal Hydrogen Sulphates, and the Mechanism of Conduction in Sulphuric Acid.—The conclusion drawn from transport-number measurements (Part X), *viz.*, that the conductivity of all basic solutes, *i.e.*, solutes that ionise as hydrogen sulphates, is due almost entirely to the chain conduction of the hydrogen sulphate ion, appears to suggest that all such solutes should have very similar conductivities. It is immediately apparent, however, from Fig. 1 and from the values of the equivalent conductivities listed in Table 5 that this is not so. The differences between the conductivities of these solutes are much too large to be attributed, as Hantzsch suggested, to the small differences between the mobilities of their cations, and it must therefore be concluded that the mobility of the hydrogen sulphate ion depends on the nature of the cation.

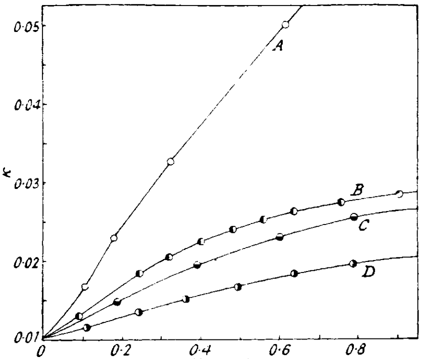
It may also be seen from the results in Table 5 that Hantzsch's conclusion that the equivalent conductivities of these solutes were constant and independent of concentration is incorrect, for there is a steady and marked decrease in the equivalent conductivity with increasing concentration in each case. This is also apparent from the shape of the specific conductivity–concentration curves in Fig. 1. In each case there is an initial curvature convex to the concentration axis due to the repression of the self-ionisation by the added solute followed by a curvature in the opposite direction. The fact that in the latter region the specific conductivity does not increase linearly with concentration but rather more slowly indicates that the equivalent conductivity of the electrolyte is decreasing, *i.e.*, the mobility of the hydrogen sulphate ion decreases with increasing concentration.* Thus

FIG. 3. *Specific conductivities of some organic solutes.*



A, NH_4HSO_4. *B*, $COMe_2$. *C*, AcOH. *D*, $Ph{\cdot}CO_2H$

FIG. 4. *Specific conductivities of some weak electrolytes.*



A, $NH_4{\cdot}HSO_4$. *B*, $p\text{-}C_6H_4Me{\cdot}NO_2$. *C*, $H_2S_2O_7$. *D*, $CHCl_2{\cdot}CO_2H$.

TABLE 5. *Equivalent conductivities of some alkali and alkaline-earth metal hydrogen sulphates.*

	NH_4HSO_4		$KHSO_4$		$NaHSO_4$		$LiHSO_4$		$Ba(HSO_4)_2$		$Sr(HSO_4)_2$	
N	100κ	Λ	100κ	Λ	100κ	Λ	100κ	Λ	100κ	Λ	100κ	Λ
0·1	1·58	158	1·56	156	1·52	152	1·52	152	1·52	152	1·52	152
0·2	2·40	120	2·32	116	2·18	109	2·17	108	2·16	105	2·10	105
0·3	3·16	105	3·02	101	2·86	95·3	2·80	93·3	2·68	89·3	2·68	89·3
0·4	3·81	95·3	3·64	91·0	3·44	86·0	3·37	84·2	3·18	79·5	3·18	79·5
0·6	4·93	82·2	4·66	77·7	4·38	73·0	4·24	70·7	3·95	65·8	3·95	65·8
0·8	5·88	73·5	5·55	69·4	5·04	63·0	4·80	60·0	4·41	55·1	4·41	55·1
1·0	6·63	66·3	6·28	62·8	5·59	55·9	5·33	53·3	4·76	47·6	4·73	47·3
1·2	7·30	60·8	6·84	57·0	6·06	50·5	5·57	46·4	5·00	41·7	4·94	41·2
1·4	7·92	56·6	7·21	51·5	6·38	47·8	5·80	41·4	5·16	36·9	5·10	36·4

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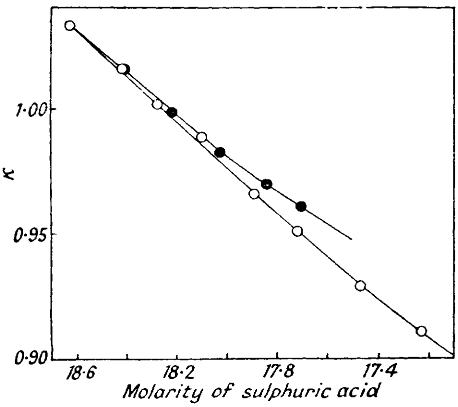
* We shall assume that all the solutes we are at present considering behave as completely strong electrolytes. This seems reasonable in view of the very probable high dielectric constant of sulphuric acid (cf. Part I) which would make incomplete ionisation or ion-pair formation very unlikely.

we may conclude that the mobility of the hydrogen sulphate ion depends on its concentration and also on the nature of the cation. The similar dependence of the mobility of an ion in aqueous solution on its concentration and the nature of the other ions present is attributed on the Debye–Hückel–Onsager theory to interionic forces. However, it is certain that the electrophoretic and relaxation effects of that theory are not the only factors influencing the mobility of an ion that conducts by a chain mechanism, and it seems probable that they may be of very little importance. It is difficult, for example, to imagine how the electrophoretic effect could apply to chain-conduction in which there is no actual movement of any individual ion. Moreover, cryoscopic measurements have shown that certainly up to concentrations of 0·5N, and probably even higher, interionic forces appear to be negligible (Hammett and Deyrup, *J. Amer. Chem. Soc.*, 1933, **55**, 1900; and Part I).

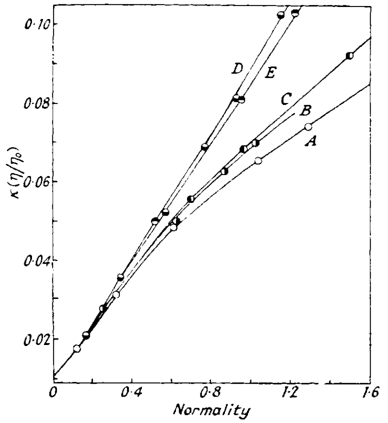
There are at least two additional factors that must influence the mobility of an ion that conducts by a chain mechanism. In discussing these we shall assume that molecular rotation and not proton transfer is the rate-determining process of chain conduction. Some evidence that this assumption is correct has already been presented in Part X, and additional evidence is given later. One of these additional factors arises from the solvation of the ions. The solvent molecules taking part in this solvation will be more or less tightly held by the ions, and their freedom of motion will be considerably restricted. In particular, they will less easily be able to rotate and will therefore play a correspondingly smaller part in the process of chain conduction. Alternatively, ion solvation may be said slightly to increase the average time of rotation of the sulphuric acid molecules and thus correspondingly reduce the hydrogen sulphate ion mobility. It follows that the greater the degree of solvation of the ions of the solute the smaller should be the specific conductivity of that solute at any given concentration. The hydrogen sulphate ion is common to all the solutes we are considering, and so, for the purposes of comparison, we do not need to take its solvation into account. The relative extent of solvation of the alkali and alkaline-earth metal cations has been determined by means of cryoscopic, density, and transport-number measurements (Parts I, X, and XI, *locc. cit.*), and found to be

FIG. 5. *Specific conductivities of sulphuryl chloride and trichloroacetic acid.*



lower curve, SO_2Cl_2.
upper curve, $CCl_3{\cdot}CO_2H$.

FIG. 6. *Specific conductivity–relative viscosity product for some alkali and alkaline-earth metal hydrogen sulphates.*



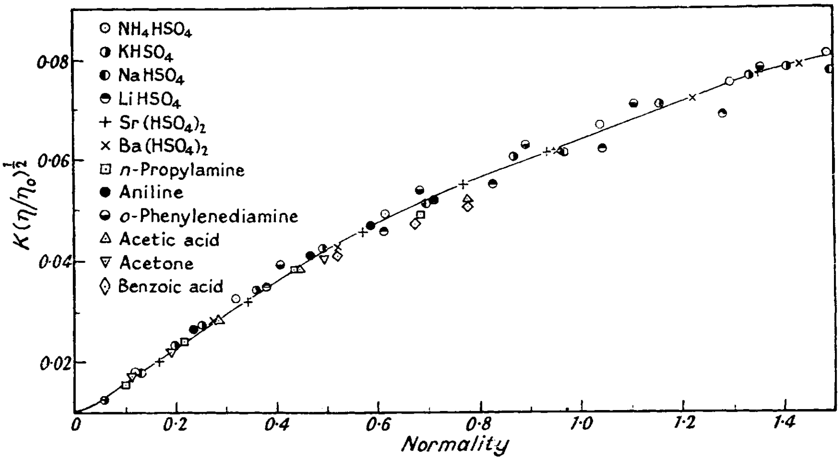
A, $NH_4{\cdot}HSO_4$. *D*, $Sr(HSO_4)_2$.
B, $KHSO_4$. *E*, $Ba(HSO_4)_2$.
C, $NaHSO_4$.

$$NH_4^+ < K^+ < Na^+ < Li^+ < Ba^{++} < Sr^{++}$$

which is also the order which would be expected on the assumption that the extent of solvation increases with increasing polarising power of the ion, and is exactly the order of decreasing conductivity of solutions of their hydrogen sulphates. As has been pointed out in Part XI (*loc. cit.*) the varying degrees of solvation of these ions are also reflected in the viscosities of solutions of their hydrogen sulphates, the restriction of the motion of these solvent molecules taking part in solvation causing an increase in the viscosity of the solution, and the order of increasing viscosity of these solutions is exactly that of increasing solvation of the cations given above.

For normal conduction by diffusion, Stokes's law is usually assumed to hold, from which it follows that the mobility of an ion is inversely proportional to the viscosity of the solution, and this conclusion has been shown to be reasonably correct for a number of different ions and solvents. An attempt to correct our observed conductivities to allow for viscosity changes on this basis, by multiplying the specific conductivity κ by the relative viscosity η/η_0 (where η is the viscosity of the solution and η_0 that of the pure solvent), gave obviously incorrect results. As can be seen from Fig. 6, the order of the conductivities has been completely reversed and they are still all quite diffierent. However, this is not really surprising as although Stokes's law may well hold for normal conduction by diffusion, it cannot be expected to apply to conduction by the quite different chain mechanism. However, it was found that to a fair approximation the conductivity was inversely proportional to the square root of the viscosity of the solution. By plotting $\kappa(\eta/\eta_0)^{\frac{1}{2}}$ against concentration a nearly common curve was obtained for a large number of electrolytes, as shown in Fig. 7. It is not certain that this result has any fundamental significance and the relationship is in any case only approximate; but the fact that the mobility is in any way related to the viscosity provides support for the assumption that molecular rotation and not proton transfer is rate-determining, as it is difficult to see how the rate of proton transfer could be much affected by the viscosity of the medium.

FIG. 7. *Corrected specific conductivities.*



The second of the additional factors that will influence the mobility of an ion that conducts by a chain mechanism arises from collisions between conducting chains. Each collision between two chains will result in a decrease in the average mobility of the chain-conducting ion. Consider the situation that arises when two hydrogen sulphate ions, each one part of a conducting chain, arrive simultaneously at positions adjacent to the same sulphuric acid molecule :

$$\begin{array}{ccc} HSO_4^- & & H_2SO_4 \\ & H_2SO_4 & \\ HSO_4^- & & H_2SO_4 \end{array}$$

One chain can pass on through the sulphuric acid molecule as soon as it becomes correctly orientated, but the other chain must wait until the sulphuric acid molecule has played its part in the first chain and then re-orientated itself to take part in the second. Thus as far as this second chain is concerned the average time of rotation of this sulphuric acid molecule has increased and the average mobility of the hydrogen sulphate ion in this chain is decreased accordingly. The greater the concentration of hydrogen sulphate ions the more frequent will such collisions be, and hence the more will the mobility of the hydrogen sulphate ion be decreased.

Hence, the solvation effect determines a decrease of mobility of the hydrogen sulphate ion with increasing concentration which is specific for each cation, while chain collisions determine a general decrease of mobility of the hydrogen sulphate ion with increasing concentration. The general agreement of these conclusions with our exprimental results provides additional justification of our original assumption that molecular rotation is the rate-determining stage of chain conduction in sulphuric acid. It would seem to be much more difficult to account for the observed effects of different cations and of concentration on the mobility of the hydrogen sulphate ion if proton transfer were the rate-determining process.

A comparison of the equivalent conductivity values in Table 4 with some equivalent conductivities in aqueous solutions is of interest. In a 0·1N-solution in water at 25° the equivalent conductivity of hydrochloric acid is 391, of sodium hydroxide 221, and of potassium chloride 129. In sulphuric acid at 25° the equivalent conductivity of, *e.g.*, potassium hydrogen sulphate is 156, and the transport number of the potassium ion being taken as 0·03 (Table 1, Part X), this means that the equivalent conductivity of the potassium ion is approximately 5, and that of the hydrogen sulphate ion approximately 150. Thus it is not that the hydrogen sulphate ion in sulphuric acid has such an abnormally high mobility, but rather that cations such as the potassium ion have abnormally small mobilities, because of the high viscosity of sulphuric acid, which causes the transport number of the hydrogen sulphate ion to be so very near to unity. If one assumes that proton transfer is easier the stronger the hydrogen bonding in the liquid, then one would expect proton transfer to be easier in sulphuric acid than in water, and if proton transfer were the rate-determining step of chain conduction in both cases the mobility of the hydrogen and hydrogen sulphate ions in sulphuric acid would be greater than that of the hydrogen and hydroxide ions in water. The fact that the first two ions in sulphuric acid have mobilities which are quite comparable with that of the third ion in water and rather less than that of the hydrogen ion strongly suggests that, at least in sulphuric acid, proton transfer is not rate-determining. This may be attributed to the strong hydrogen bonding in the liquid hindering molecular rotation, evidence of which is given by the high viscosity of sulphuric acid. The difference in the mobilities of the hydrogen and hydroxide ions in water moreover suggests that here proton transfer is rate-determining, or at least of comparable speed to molecular rotation.

The Conductivities of Some Strong Electrolytes.—Extensive use has been made of the cryoscopic method for investigating the ionisation of solutes in sulphuric acid (cf. Parts I—VIII and references given therein). Not only does sulphuric acid have a convenient freezing point and other properties that make the experimental technique relatively simple, but the apparent ideality of the solutions considerably simplifies the interpretation of the results and enables a relatively accurate estimate of the degree of ionisation of a solute to be made. It is obvious, however, from the results so far discussed, that conductivity measurements cannot be so useful in this connection as cryoscopy has been. Whereas all electrolytes of the same valency type have almost exactly the same freezing-point depression, they may, as we have seen, have quite appreciably different conductivities. Moreover, in order to calculate equivalent or molar conductivities it is necessary to know the densities of the solutions, which involves making another measurement in addition to that of the conductivity. The assumption, that might be made for simplicity, that the densities of solutions are the same as that of the pure solvent may be only very approximately true at the relatively high concentrations at which it is necessary to work. Thus if this assumption is made it is another factor contributing towards the difference between the conductivities of electrolytes of the same valency type. Conductivity measurements can therefore only be used to differentiate between different possible modes of ionisation of a solute and not to determine exact or even approximate degrees of ionisation. Since the conductivity of any basic solute in sulphuric acid is due almost exclusively to the hydrogen sulphate ion, the information that can be obtained from a determination of the conductivity of a solute is the number of hydrogen sulphate ions produced by the ionisation of one molecule of the solute. This may provide a useful check on conclusions drawn from a cryoscopic investigation of the ionisation of a solute, since this method enables one to find the total number of particles, both ionised and un-ionised, produced on dissolution of one molecule of the solute.

It will be convenient for our discussion to classify basic solutes in terms of the number of hydrogen sulphate ions produced by the ionisation of one molecule of the solute, and we shall therefore consider mono-, di-, tri-, and tetra-(hydrogen sulphates) in turn.

The specific conductivity curves in Figs. 2 and 3 and the molar conductivities given in Table 6 for water, acetic acid, acetone, benzoic acid, *n*-propylamine, aniline, methyl alcohol, and ethyl alcohol are sufficiently close to the corresponding specific and molecular conductivities of the alkali-metal hydrogen sulphates to justify the conclusion that one molecule of each of these solutes produces one hydrogen sulphate ion in solution. Cryoscopic measurements have shown that acetic acid and acetone (Part I) and benzoic acid (Gillespie, unpublished experiments) produce exactly two particles per molecule up to a concentration of 0·4N, suggesting that they are fully ionised according to the equation $B + H_2SO_4 = BH^+ + HSO_4^-$. The conductivity results are in full agreement with this conclusion, and show in addition that at concentrations greater than 0·4N the ionisation must still be considerable if not complete, although they provide no exact information about this.

Cryoscopic measurements (Part II) have shown that water is approximately 90% ionised in a 0·2N-solution and correspondingly less ionised at higher concentrations according to the equation $H_2O + H_2SO_4 = H_3O^+ + HSO_4^-$. The conductivity results are in agreement with this conclusion, although one could not have concluded from these alone that the ionisation was incomplete.

TABLE 6. *Molar conductivities at 25°.*

Mono(hydrogen sulphates).*

M	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
0·1	158	155	156	155	156	156	152	155	152	152
0·2	120	120	115	120	117	117	116	120	108	113
0·3	105	102	100	102	103	101	99·3	102	93·3	96·3
0·4	95·3	92·5	90·3	91·5	93·8	91·8	89·5	91·5	84·2	86·0
0·6	82·2	80·1	78·3	79·3	79·8	78·3	77·1	77·7	70·7	72·0
0·8	73·5	72·4	70·0	70·5	70·1	69·5	67·9	67·2	60·0	61·1
1·0	66·3	63·9	63·2	62·9	62·2	61·9	59·8	59·1	53·3	52·6

Di(hydrogen sulphates).

M	(11)	(12)	(13)	(14)
0·05	306	300	306	304
0·10	229	229	236	21
0·15	197	—	201	179
0·20	177	—	187	150
0·30	155	—	153	132
0·40	138	—	130	110
0·50	125	—	119	95

Tri(hydrogen sulphate).

M	(15)
0·033	453
0·066	336
0·100	296
0·133	268

Tetra(hydrogen sulphate).

M	(16)
0·025	616
0·050	454
0·075	388
0·100	349

* (1) NH_4HSO_4. (2) $COMe_2$. (3) H_2O. (4) NH_2Pr^n. (5) EtOH. (6) MeOH. (7) $CH_3{\cdot}CO_2H$. (8) NH_2Ph. (9) $LiHSO_4$. (10) $Ph{\cdot}CO_2H$. (11) HNO_3. (12) $CPh_3{\cdot}OH$. (13) *o*-$C_6H_4(NH_2)_2$. (14) $Ba(HSO_4)_2$. (15) N_2O_4. (16) Hexamethylenetetramine.

The ionisation of *n*-propylamine and aniline was investigated by Oddo and Scandola (*Gazzetta*, 1909, **39**, i, 569), whose relatively crude cryoscopic measurements showed extensive if not complete ionisation as simple bases. Our present conductivity results are in full agreement with this conclusion.

It has been shown by cryoscopic measurements (Part VII) that methyl and ethyl alcohol each ionise according to the equation

$$ROH + 2H_2SO_4 = RHSO_4 + H_3O^+ + HSO_4^-$$

with in addition, perhaps, a very slight basic ionisation of the alkyl hydrogen sulphate

$$RSO_4H + H_2SO_4 = RSO_4H_2^+ + HSO_4^-$$

The conclusion from the conductivity results that one hydrogen sulphate ion is formed on the ionisation of one molecule of each of these alcohols is in full accord with this interpretation of the cryoscopic results.

A comparison of the molar conductivities of nitric acid, *o*-phenylenediamine, and triphenylmethanol (Table 6) with those of barium and strontium di(hydrogen sulphate) shows that all these solutes ionise to give two hydrogen sulphate ions. By cryoscopic, spectroscopic, and other methods, nitric acid has been shown to be converted into fully ionised nitronium hydrogen sulphate and almost fully ionised hydroxonium hydrogen sulphate (Gillespie and Millen, *Quart. Reviews*, 1948, **2**, 277). This can be best represented by the equation

$$HNO_3 + 2H_2SO_4 = NO_2^+ + H_3O^+ + 2HSO_4^-$$

The present conductivity results are in complete accord with this conclusion. There has been no previous study of *o*-phenylenediamine, but our results indicate that it is extensively if not completely ionised according to the equation

$$C_6H_4(NH_2)_2 + 2H_2SO_4 = [C_6H_4(NH_3)_2]^{++} + 2HSO_4^-$$

The ionisation of triphenylmethanol has been investigated cryoscopically by Hammett and Deyrup (*J. Amer. Chem. Soc.*, 1933, **55**, 1900), who found that it gave almost exactly four particles. This result has been explained as being due to the ionisation

$$Ph_3C{\cdot}OH + 2H_2SO_4 = Ph_3C^+ + H_3O^+ + 2HSO_4^-$$

with which our conductivity results are in complete agreement. It is noteworthy that although the ionisation of *o*-phenylenediamine gives rise to only three ions while nitric acid and triphenylmethanol give four ions, they all have very nearly the same conductivity. This is due, of course, to the fact that the conductivity is due almost entirely to the hydrogen sulphate ion, and two hydrogen sulphate ions result from the ionisation of each of these solutes.

The only tri(hydrogen sulphate) that we have investigated is dinitrogen tetroxide which has been found cryoscopically (Part III) to give nearly six particles and has therefore been assumed to ionise according to the equation

$$N_2O_4 + 3H_2SO_4 = NO^+ + NO_2^+ + H_3O^+ + 3HSO_4^-$$

The fact that the values of its molar conductivity are greater than those for the di(hydrogen sulphates) and are in fact to quite a good approximation three times those for the mono(hydrogen sulphates) at the same hydrogen sulphate ion concentrations provides further support for the above mode of ionisation for dinitrogen tetroxide.

Hexamethylenetetramine does not appear to have been previously investigated. It has molar conductivity values that are greater again than those for dinitrogen tetroxide and are approximately four times the average values for a mono(hydrogen sulphate), strongly suggesting that four hydrogen sulphate ions result from its ionisation, which may accordingly be represented by the equation

$$C_6H_{12}N_4 + 4H_2SO_4 = [C_6H_{12}N_4H_4]^{4+} + 4HSO_4^-$$

At the present stage of our knowledge of solutions in sulphuric acid, little can be said about the differences between the conductivities of the organic mono(hydrogen sulphates), the only class of organic compounds that we have studied at all extensively. If we can discount the possibility that organic solutes have some specific effect which causes an increase in the mobility of the hydrogen sulphate ion, then it would appear from a comparison with the molar conductivities of ammonium and lithium hydrogen sulphates that the cations of all the solutes we have studied are more solvated than the ammonium ion and less solvated than the lithium ion. This conclusion is in fair agreement with that drawn from the results of cryoscopic measurement (Part I), *viz.*, that the ammonium ion and the cations of acetone and acetic acid all have solvation numbers of approximately unity. It is possible, however, that the disruption of the structure of the sulphuric acid by large organic cations enables some sulphuric acid molecules to rotate more easily, and thus increases the mobility of the hydrogen sulphate ion.

The Conductivities of Some Weak Electrolytes and Some Non-electrolytes.—We have investigated the conductivities of solutions of three solutes, *p*-nitrotoluene, disulphuric acid, and dichloroacetic acid, that have been shown by cryoscopy to behave as weak electrolytes (Hantzsch, *loc. cit.*; and Parts II and VII). The results of these measurements have been given in Table 3 and in Fig. 4. No values for the molar conductivities of these solutes have been given, for up to almost the highest concentrations we have investigated, particularly in the cases of disulphuric acid and dichloroacetic acid, the repression of the autoprotolysis of the solvent is appreciably incomplete. Moreover, as already pointed out, such values would be of little use since, in view of the differences between the conductivities of solutes that are known to be fully ionised, they could only be used to calculate approximate degrees of ionisation. It is probably justifiable to conclude from the conductivity–concentration curves in Fig. 4 that the extent of ionisation of these solutes increases in the order dichloroacetic acid < disulphuric acid < *p*-nitrotoluene, which is in agreement with the results of the cryoscopic measurements. Hantzsch (*loc. cit.*) showed that dichloroacetic acid is approximately 20% ionised in roughly the same concentration range as we have used, and in Part VII it was shown that *p*-nitrotoluene is 73% ionised in a 0·1m-solution. The ionisation of disulphuric acid is slightly complicated by the formation of higher polysulphuric acids, such as trisulphuric acid ($H_2S_3O_{10}$), but if this complication is ignored, cryoscopic measurements show that disulphuric acid is 38% ionised in a 0·1m-solution. It is justifiable to compare the acidic solute disulphuric acid with the two basic solutes, for it has been shown in Part IX that the mobility of the hydrogen ion ($H_3SO_4^+$) is very nearly if not exactly equal to that of the hydrogen sulphate ion.

Solutions of non-electrolytes in sulphuric acid will of course have a conductivity due to the hydrogen and hydrogen sulphate ions arising from the autoprotolysis of the solvent. We have investigated two solutes that have been regarded from freezing-point depression measurements as behaving as non-electrolytes, *viz.*, sulphuryl chloride, studied by Gillespie, Hughes, and Ingold (Part I), and trichloroacetic acid, studied by Hantzsch (*loc. cit.*) and by Hammett and Deyrup (*J. Amer. Chem. Soc.*, 1933, **55**, 1900). A number of other solutes which were regarded by Hantzsch and by Hammett and Deyrup as behaving as non-electrolytes have been shown cryoscopically to be weak electrolytes (Parts I and VII). The results of our experiments with these two solutes have been given in Table 3 and Fig. 5. It may be seen that in both cases the conductivity of the solution decreases slightly with increasing concentration of the solute. Such a decrease in conductivity would be expected because of the dilution of the conducting sulphuric acid by the non-conducting solute. If this were the only effect operating to reduce the conductivity of the solution, the specific conductivity should decrease linearly with the molarity of sulphuric acid in the solution with a slope of $\kappa_0/c_0 = 5{\cdot}55 \times 10^{-4}$, where κ_0 is the specific conductivity of pure sulphuric acid and c_0 its molarity (lower curve on Fig. 5). In fact, as may be seen from Fig. 5, the specific conductivity does decrease linearly with the molarity of sulphuric acid in the case of sulphuryl chloride, although the slope of the straight line is considerably greater, namely, $9{\cdot}2 \times 10^{-4}$. This additional decrease in the specific conductivity may be attributed either to a decrease in the extent of autoprotolysis of the solvent owing to a decreased ionising power or dielectric constant of the solution, or to a decrease in the mobility of the hydrogen or hydrogen sulphate ions, or to both. The specific conductivity of solutions of trichloroacetic acid does not decrease linearly with the molarity of sulphuric acid, and at all concentrations the conductivities are slightly greater than those for sulphuryl chloride. This may be due either to a different effect of trichloroacetic acid on the extent of autoprotolysis or on the mobility of the hydrogen and hydrogen sulphate ions, or to a very slight ionisation of trichloroacetic acid as a base. In view of the basic properties of dichloroacetic acid, it is not unreasonable to suppose that trichloroacetic acid will also be basic if only to a very limited extent.

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