841. *Solutions in Sulphuric Acid. Part XXX.* Conductivities of Some Electrolyte Solutions: Metal Sulphates, Ketones, and Tetra-(hydrogen sulphato)boric Acid.*

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The results of measurements of the electrical conductivities of solutions of metal sulphates, ketones, and tetra(hydrogen sulphato)boric acid are reported.

In continuation of our studies of solutions in sulphuric acid, and in particular of the mechanism of electrical conduction in this solvent, we have extended our earlier measurements [1] of the electrical conductivities of electrolyte solutions to include all the metal sulphates that are sufficiently soluble, some ketones, and tetra(hydrogen sulphato)boric acid. Some of these data were needed for the conductometric analysis of solutions in the equilibrium cryoscopic measurements described in Part XXVI.[2]

The solubilities of metal sulphates in sulphuric acid have been studied by Kendall and Davidson.[3] In agreement with their observations, we found from a study of a large number of metal sulphates, that, in addition to the sulphates of Li, Na, K, NH_4, Ba, and Sr, whose conductivities had been measured previously,[1] only the sulphates of Rb, Cs, Ag, Tl(I), Ca, Pb(II), and Hg(I) are sufficiently soluble to cause an appreciable change in the conductivity. In the present work the conductivities of all these metal sulphates,

Table 1. *Specific conductances of some electrolyte solutions* (25°).

w	$10^2\kappa$	w	$10^2\kappa$	w	$10^2\kappa$	w	$10^2\kappa$	w	$10^2\kappa$
$LiHSO_4$		$KHSO_4$		$KHSO_4$ (cont.)		$RbHSO_4$ (cont.)		$AgHSO_4$ (cont.)	
0·0106	1·067	0·0048	1·0505	0·0129	1·087	0·3313	4·955	0·0595	1·623
0·0298	1·218	0·0194	1·354	0·0299	1·240	0·4868	6·212	0·1033	2·246
0·0713	1·735	0·0676	1·740	0·0558	1·573			0·1558	2·942
0·1089	2·222	0·1221	2·503	0·0849	1·986	$CsHSO_4$		0·1864	3·315
0·1775	3·001	0·1761	3·195	0·1196	2·469	0·0242	1·190	0·2531	4·052
0·2939	4·005	0·2193	3·681	0·1627	3·030	0·0470	1·482	0·4096	5·427
0·0157	1·098	0·2596	4·115	0·2419	3·931	0·0670	1·776	0·0110	1·0764
0·0438	1·383	0·2973	4·506	0·3277	4·752	0·1100	2·425	0·0332	1·277
0·0814	1·875	0·0025	1·0458	0·4723	5·856	0·1508	3·011	0·0554	1·560
0·1743	2·971	0·0259	1·1962			0·2092	3·780	0·0851	1·967
0·2388	3·576	0·0357	1·308	$RbHSO_4$		0·2580	4·361	0·1172	2·426
0·3338	4·277	0·0577	1·597	0·0003	1·0438	0·0236	1·192	0·1337	2·645
0·4319	4·824	0·0840	1·974	0·0005	1·0438	0·0508	1·550	0·1749	3·163
		0·1086	2·322	0·0008	1·0442	0·0750	1·905	0·2204	3·682
$NaHSO_4$		0·1339	2·665	0·0131	1·1010	0·1042	2·354	0·2547	4·044
0·0228	1·156	0·1626	3·032	0·0341	1·3262	0·1396	2·871	0·0270	1·208
0·0499	1·468	0·1903	3·365	0·0784	1·9583	0·1792	3·414	0·0584	1·594
0·1352	2·591	0·2293	3·802	0·1252	2·645	0·2384	4·414	0·0773	1·873
0·2000	3·319	0·2838	4·353	0·1954	3·555	0·2790	4·614	0·1156	2·405
0·2812	4·075	0·3457	4·907	0·2731	4·434			0·1355	2·670
0·3807	4·811	0·0007	1·044	0·3656	5·303	$AgHSO_4$		0·1715	3·122
0·0036	1·0489	0·0026	1·046	0·4775	6·182	0·0344	1·283	0·2104	3·575
0·0202	1·1327	0·0054	1·052	0·0003	1·044	0·0435	1·395	0·2647	4·147
0·0432	1·382	0·0073	1·057	0·0013	1·045	0·0617	1·642	0·3127	4·613
0·0672	1·701	0·0112	1·074	0·0095	1·068	0·0772	1·862		
0·1131	2·314	0·0206	1·140	0·0292	1·234	0·0920	2·071	$TlHSO_4$	
0·1432	2·681	0·0441	1·407	0·0436	1·415	0·1167	2·412	0·0196	1·164
0·1871	3·185	0·0754	1·842	0·0697	1·790	0·1501	2·848	0·0706	1·868
0·2252	3·594	0·1412	2·764	0·0965	2·190	0·2054	3·512	0·0924	2·201
0·3155	4·346	0·2663	4·172	0·1468	2·895	0·2688	4·178	0·1296	2·761
0·3503	4·616	0·4118	5·426	0·2335	3·958	0·4661	5·798	0·1828	3·504

* Part XXIX, *J.*, 1960, 845.

[1] Gillespie and Wasif, *J.*, 1953, 204.
[2] Bass and Gillespie, *J.*, 1960, 814.
[3] Kendall and Davidson, *J. Amer. Chem. Soc.*, 1921, **43**, 979.

TABLE 1. (*Continued.*)

w	$10^2\kappa$
$TlHSO_4$ (cont.)	
0·2720	4·610
0·3628	5·582
0·4518	6·418
0·0356	1·312
0·0604	1·670
0·0940	2·223
0·1350	2·736
0·1888	3·579
0·2632	4·501
0·3722	5·778
0·4478	6·479
0·5524	7·359
0·7472	8·638
$Ca(HSO_4)_2$	
0·0066	1·083
0·0279	1·519
0·0592	2·276
0·0925	2·958
0·1273	3·154
0·1918	4·263
0·2800	4·864
0·0262	1·454
0·0556	2·164
0·0896	2·870
0·1771	4·082
0·2882	4·864
$Sr(HSO_4)_2$	
0·0119	1·140
0·0528	2·088
0·1000	3·052
0·1577	3·871
0·2174	4·434
0·0306	1·585
0·0693	2·497
0·1120	3·281
0·1650	3·979
0·2250	4·507
$Ba(HSO_4)_2$	
0·0376	1·841
0·0695	2·650
0·1253	3·717
0·1856	4·490
0·0114	1·163
0·0379	1·840
0·0604	2·423
0·0901	3·084
0·1401	3·932
0·1980	4·612
$Pb(HSO_4)_2$	
0·0624	2·355
0·0888	2·913
0·0265	1·497
0·0640	2·416
0·0841	2·852
0·1030	3·216
$Hg_2(HSO_4)_2$	
0·0159	1·114
0·0692	1·646
0·1377	2·324

w	$10^2\kappa$
$H_3O{\cdot}HSO_4$	
0·0568	1·524
0·1055	2·228
0·2071	3·483
0·3257	4·657
0·4434	5·611
0·6029	6·670
0·8054	7·751
0·0217	1·122
0·0857	1·941
0·1382	2·672
0·1911	3·314
0·2370	3·824
0·3040	4·490
0·3802	5·141
0·0005	1·0437
0·0020	1·0433
0·0036	1·0439
0·0050	1·0453
0·0078	1·0514
0·0180	1·1023
0·0302	1·2134
0·0316	1·225
0·0481	1·436
0·0787	1·870
0·1134	2·361
0·1487	2·830
0·1814	3·234
0·2300	3·783
0·2560	4·055
0·3136	4·605
0·3320	4·774
0·4077	5·397
0·0004	1·0437
0·0014	1·0434
0·0024	1·0434
0·0035	1·0438
0·0045	1·0450
0·0070	1·0492
0·0096	1·0570
0·0155	1·0862
0·0234	1·1479
0·0399	1·332
0·0564	1·558
0·0766	1·846
0·0964	2·130
0·1171	2·469
0·1548	2·905
0·1881	3·317
0·2293	3·780
0·2916	4·410
0·3738	5·137
0·4294	5·573
$H_2S_2O_7$	
0·0011	1·0450
0·0057	1·0536
0·0168	1·0920
0·0277	1·1429
0·0382	1·200
0·0863	1·446
0·2044	1·945
0·3459	2·298
0·5091	2·749
0·0005	1·0444
0·0015	1·0454
0·0024	1·0466

w	$10^2\kappa$
$H_2S_2O_7$ (cont.)	
0·0034	1·0483
0·0044	1·0502
0·0063	1·0547
0·0090	1·0628
0·0134	1·0777
0·0176	1·0948
0·0219	1·1142
0·0502	1·259
0·0921	1·472
0·1182	1·595
0·1707	1·817
0·1884	1·885
0·1946	1·907
$HB(HSO_4)_4$	
0·0013	1·044
0·0049	1·045
0·0110	1·062
0·0172	1·103
0·0236	1·162
0·0322	1·277
0·0394	1·372
0·0015	1·044
0·0039	1·048
0·0151	1·106
0·0268	1·223
0·0425	1·413
0·0573	1·657
0·0710	1·856
0·0118	1·089
0·0218	1·181
0·0316	1·284
0·0414	1·417
0·0562	1·655
0·0796	1·965
0·0062	1·063
0·0143	1·115
0·0256	1·235
0·0327	1·262
0·0404	1·407
0·0608	1·683
0·0031	1·048
0·0076	1·055
0·0131	1·082
0·0181	1·131
0·0223	1·182
0·0507	1·525
0·0348	1·294
0·2198	3·652
0·1175	2·682
0·1060	2·475
0·1175	2·661
0·1338	2·839
0·0743	1·888
0·0557	1·620
0·0970	2·213
0·0513	1·537
0·1142	2·577
0·1228	2·719
0·2900	4·084
0·1755	3·255
0·2548	3·849
0·3201	4·208
0·2530	3·871

w	$10^2\kappa$
$NH_4{\cdot}HSO_4$	
0·0059	1·054
0·0209	1·151
0·0428	1·404
0·0657	1·726
0·1103	2·374
0·1822	3·337
0·2740	4·393
0·3826	5·441
0·0162	1·111
0·0418	1·393
0·0726	1·828
0·1007	2·238
0·1696	3·183
0·2407	4·034
0·3505	5·153
0·4824	6·256
Acetone	
0·0155	1·093
0·0360	1·286
0·0616	1·627
0·0836	1·944
0·1267	2·563
0·1608	3·024
0·0166	1·117
0·0475	1·462
0·0776	1·891
0·1040	2·273
0·1448	2·845
0·1798	3·296
0·0439	1·464
0·0784	1·456
0·1215	2·575
0·1731	3·263
0·2489	4·157
0·3605	5·246
0·4915	6·266
Acetophenone	
0·0043	1·050
0·0275	1·223
0·0472	1·471
0·0666	1·743
0·0843	1·999
0·1022	2·255
0·1422	2·804
0·1779	3·249
0·0115	1·078
0·0344	1·294
0·0562	1·588
0·0855	2·013
0·1167	2·453
0·0323	1·298
0·0905	2·126
0·1383	2·783
0·1933	3·455
0·2659	4·201
0·3725	5·057
0·4607	5·587
0·5574	6·020
Benzophenone	
0·0123	1·084
0·0491	1·492
0·0831	1·977

w	$10^2\kappa$
Benzophenone (cont.)	
0·1072	2·314
0·1491	2·852
0·0194	1·133
0·0409	1·377
0·0787	1·910
0·1111	2·359
0·1524	2·882
0·0342	1·280
0·0954	2·112
0·1547	2·864
0·2157	3·502
0·3103	4·246
0·4149	4·786
0·5125	5·084
0·0094	1·0613
0·0374	1·313
0·0596	1·610
0·0698	1·753
0·0866	1·988
0·1030	2·212
0·1189	2·425
0·1383	2·671
0·1680	3·018
0·2010	3·365
0·2377	3·704
0·2640	3·944
0·3035	4·230
0·3578	4·554
Di-*p*-tolyl ketone	
0·0188	1·125
0·0361	1·305
0·0644	1·681
0·0944	2·088
0·1320	2·561
0·0375	1·308
0·0859	1·955
0·1515	2·766
0·2483	3·653
0·1127	2·321
0·2116	3·369
0·3436	4·220
0·4940	4·647
0·5865	4·712
4,4′-Dichlorobenzophenone	
0·0107	1·072
0·0478	1·457
0·0850	1·962
0·1512	2·772
0·1437	3·203
0·2456	3·630
0·0542	1·559
0·1113	2·355
0·1630	2·973
0·2278	3·574
0·0242	1·190
0·0820	1·950
0·1348	2·621
0·1943	3·366
0·2823	3·966
0·3723	4·338
0·4717	4·531

including those studied previously, have been measured at 25°. The results are given in Table 1. As metal sulphates are quantitatively converted in solution into hydrogen sulphates, the compositions of the solutions are expressed in terms of the hydrogen sulphates. All the solutions were made up by weight, and their concentrations are given as moles of solute per kg. of solution, *i.e.*, in molon units,[4] and are denoted by the symbol w. For comparison and for use in subsequent calculations (see following paper) interpolated conductivities are required at round molal concentrations (m) and at round molar concentrations (c) and these are given in Table 2. They were obtained from large-scale

TABLE 2. *Interpolated specific conductances* (25°).

m (mole kg.$^{-1}$ of solvent)	0·01	0·02	0·03	0·04	0·06	0·08	0·10	0·14	0·18	0·24	0·32	0·40
$LiHSO_4$	1·065	1·125	1·224	1·336	1·582	1·838	2·101	2·60	3·02	3·56	4·15	—
$NaHSO_4$	1·067	1·133	1·229	1·342	1·600	1·862	2·128	2·63	3·07	3·67	4·29	—
$KHSO_4$	1·068	1·139	1·240	1·356	1·626	1·900	2·176	2·71	3·19	3·84	4·57	—
$RbHSO_4$	1·068	1·152	1·260	1·390	1·670	1·962	2·260	2·82	3·34	4·08	4·88	5·58
$CsHSO_4$	1·068	1·152	1·260	1·390	1·672	1·984	2·290	2·88	3·42	4·17	5·05	5·78
$AgHSO_4$	1·067	1·142	1·235	1·348	1·608	1·880	2·157	2·67	3·13	3·78	4·46	—
$TlHSO_4$	1·068	1·152	1·260	1·390	1·680	2·009	2·324	2·91	3·46	4·23	5·15	5·87
$NH_4{\cdot}HSO_4$	1·068	1·142	1·247	1·365	1·635	1·927	2·215	2·76	3·26	3·95	—	—
$Ca(HSO_4)_2$	1·135	1·352	1·587	1·823	2·31	2·72	3·08	3·58	4·08	—	—	—
$Sr(HSO_4)_2$	1·135	1·342	1·570	1·802	2·26	2·67	3·02	3·52	4·02	4·50	—	—
$Ba(HSO_4)_2$	1·135	1·374	1·626	1·876	2·38	2·83	3·22	3·78	4·32	—	—	—
$H_3O{\cdot}HSO_4$	1·0584	1·1172	1·209	1·329	1·601	1·879	2·162	2·686	3·174	3·822	4·562	5·198
$H_2S_2O_7$	1·0635	1·1047	1·154	1·204	1·307	1·407	1·502	1·676	1·830	2·033	2·260	2·45
$HB(HSO_4)_4$	1·067	1·145	1·250	1·375	1·665	1·970	2·29	2·81	3·19	3·61	4·04	4·30

c (mole l.$^{-1}$)	0·01	0·02	0·04	0·06	0·10	0·20	0·30	0·40	0·50	0·60	0·70	0·80
$LiHSO_4$	1·050	1·068	1·145	1·252	1·520	2·23	2·86	3·39	3·85	4·23	4·56	4·84
$NaHSO_4$	1·051	1·068	1·147	1·258	1·536	2·26	2·92	3·49	3·99	4·77	4·79	5·12
$KHSO_4$	1·052	1·073	1·156	1·274	1·558	2·33	3·04	3·68	4·23	4·72	5·16	5·56
$RbHSO_4$	1·052	1·08	1·17	1·29	1·61	2·40	3·14	3·77	4·40	4·84	5·37	—
$CsHSO_4$	1·052	1·08	1·17	1·29	1·61	2·41	3·15	3·79	4·47	5·00	5·51	—
$AgHSO_4$	1·053	1·075	1·16	1·26	1·55	2·29	3·00	3·62	4·15	4·62	5·07	5·48
$TlHSO_4$	1·053	1·08	1·17	1·29	1·61	2·45	3·19	3·87	4·48	5·01	5·52	—
NH_4HSO_4	1·053	1·075	1·161	1·278	1·590	2·38	3·11	3·79	4·39	4·94	5·44	—
$H_3O{\cdot}HSO_4$	1·046	1·061	1·130	1·249	1·530	2·284	2·994	3·60	4·15	4·63	5·07	5·44
$H_2S_2O_7$	1·054	1·068	1·114	1·169	1·281	1·553	1·788	1·991	2·17	2·33	2·47	—
$HB(HSO_4)_4$	1·051	1·073	1·163	1·29	1·61	2·39	3·12	3·60	3·99	4·23	4·32	—
$(CH_3)_2CO$	1·052	1·073	1·153	1·270	1·56	2·35	3·11	3·80	4·46	5·01	—	—
$CH_3{\cdot}CO{\cdot}C_6H_5$	1·052	1·073	1·153	1·270	1·56	2·35	3·11	3·75	4·32	4·79	—	—
$(C_6H_5)_2CO$	1·052	1·073	1·153	1·270	1·56	2·34	3·01	3·58	4·04	4·42	4·72	—
$(p\text{-}CH_3{\cdot}C_6H_4)_2CO$	1·052	1·073	1·153	1·270	1·55	2·29	2·47	3·48	3·88	4·23	4·54	—
$(p\text{-}Cl{\cdot}C_6H_4)_2CO$	1·052	1·073	1·153	1·270	1·56	2·30	2·48	3·49	3·88	—	—	—

plots of κ against w by interpolation at the appropriate w values calculated from the expressions $w = c/\rho$ and $w = \mathrm{m}/(1 + \mathrm{m}W/1000)$ where ρ is the density of the solution [5] and W is the molecular weight of the solute. New measurements were also made of the conductivities of solutions of water which behaves as the strong binary electrolyte, oxonium hydrogen sulphate, $H_3O{\cdot}HSO_4$. Since these new measurements led to some slight revisions of the interpolated values reported previously,[6] and since they were also useful for comparison and for calculations reported in following papers, the new values are also included in Tables 1 and 2.

The conductivities of solutions of some organic bases have been reported previously.[1] These measurements have now been extended to include a series of ketones of varying molecular size in order to investigate the effect of ion size on the conductivity. The large size of some organic cations has been found to be responsible for the considerable deviations from ideality in the freezing points of their solutions.[2,7] The conductivities at 25° of

[4] Gillespie and Solomons, *J. Chem. Educ.*, 1960, **37**, 202.
[5] Flowers, Gillespie, and Robinson, *J.*, 1960, 845.
[6] Gillespie, Oubridge, and Solomons, *J.*, 1957, 1804.
[7] Bass, Gillespie, and Oubridge, *J.*, 1960, 837.

acetone, acetophenone, benzophenone, 4,4′-dimethyl- and 4,4′-dichloro-benzophenone are given in Tables 1 and 2.

The conductivities of solutions of metal sulphates and organic bases are due very largely to the hydrogen sulphate ion.[1] It is also of importance to have information on the conductivities of solutions containing the hydrogen ($H_3SO_4^+$) ion, *i.e.*, "acidic" solutions in the sulphuric acid solvent system. Conductivities of solutions of the strong acid, tetra(hydrogen sulphato)boric acid $HB(HSO_4)_4$,[8] are therefore also given in Table 1 together with values for the weaker disulphuric acid. Conductivities of solutions of disulphuric acid have been reported previously,[6] but further measurements have, as in the case of water, necessitated some slight changes in the interpolated values, so that new values are given here. The accuracy of the results for tetra(hydrogen sulphato)boric acid is probably not as great as for the other electrolytes studied, since solutions of accurately known composition are difficult to prepare. It was necessary to measure the concentration of a disulphuric acid solution by means of its conductivity and then to add an exact amount of boric acid calculated according to the equation,[8] $H_3BO_3 + 3H_2S_2O_7 = HB(HSO_4)_4 + 2H_2SO_4$.

In addition, the conductivities of solutions of potassium sulphate, tetra(hydrogen sulphato)boric acid, water, and disulphuric acid were measured at 10°, and measurements were also made on potassium sulphate solutions at 40°. The results of these measurements are given in Table 3.

TABLE 3. *Specific conductances at* 10° *and* 40°.

w	$10^2\kappa$
H_2O (10·30°)	
0·0045	0·5873
0·0079	0·5924
0·0162	0·6084
0·0206	0·652
0·0287	0·715
0·0451	0·865
0·0692	1·119
0·0095	1·587
0·0131	0·611
0·0257	0·690
0·0339	0·758
0·0585	1·012
0·0284	0·671
0·0336	0·754
0·0057	0·586
0·0210	0·650
0·0324	0·739
0·0491	0·906
0·1782	1·035
0·0031	0·592
0·0104	0·600
0·0329	0·741
0·0451	0·864
0·0656	1·068
0·0976	1·128
0·1206	1·408
0·1368	1·634
0·1548	1·771
0·1688	1·970

w	$10^2\kappa$
$H_2S_2O_7$ (10·30°)	
0·0004	0·5871
0·0040	0·5919
0·0080	0·6019
0·0124	0·6156
0·0784	0·8611
0·1487	1·0793
0·1852	1·170
0·3212	1·478
0·3940	1·004
0·6685	1·422
0·6855	1·466
0·7040	2·052
0·0012	0·588
0·0068	0·599
0·0154	0·621
0·0756	0·851
0·1355	1·037
0·2750	1·394
0·2955	1·402
0·0402	0·7399
0·0515	0·7611
0·0679	0·8235
0·0846	0·8971
0·1384	1·047
0·4330	1·635
0·5195	1·775
0·5970	1·862
0·0060	0·600
0·0180	0·647
0·0410	0·764
0·0792	0·866
0·1225	1·003

w	$10^2\kappa$
$H_2S_2O_7$ (10·30°) (cont.)	
0·1990	1·208
0·2980	1·438
0·4126	1·627
0·5170	1·771
0·7060	1·468
0·0120	0·609
0·0415	0·724
0·0614	0·800
0·1125	0·972
0·1979	1·202
0·2810	1·402
0·5976	1·863
0·6950	2·020
0·7230	2·095
$HB(HSO_4)_4$ (10·30°)	
0·0013	0·5863
0·0048	0·5864
0·0109	0·6062
0·0171	0·6435
0·0235	0·6977
0·0321	0·7960
0·0393	0·8745
0·0015	0·5868
0·0150	0·6467
0·0267	0·7502
0·0425	0·9078
0·0573	1·096
0·0709	1·243
0·0118	0·6328

w	$10^2\kappa$
$HB(HSO_4)_4$ (10·30°) (cont.)	
0·0218	0·7144
0·0310	0·8039
0·0414	0·9098
0·0562	1·093
0·0796	1·318
0·0066	0·6070
0·0142	0·6544
0·0560	0·7605
0·0326	0·8234
0·0404	0·9016
0·0607	1·115
0·0075	0·603
0·0131	0·624
0·0181	0·669
0·0223	0·713
$KHSO_4$ (10·30°)	
0·0080	0·5986
0·0290	0·7326
0·0361	0·7951
0·0443	0·8736
0·0578	1·016
0·0888	1·327
0·0357	0·7901
0·0666	1·073
0·0896	1·333
0·1011	1·450
0·0134	0·6228
0·0534	0·9701
0·0791	1·225

w	$10^2\kappa$
$KHSO_4$ (10·30°) (cont.)	
0·0834	1·268
0·0967	1·405
0·1050	1·442
$KHSO_4$ (9·92°)	
0·0109	0·592
0·0360	0·765
0·0985	1·380
0·1732	2·044
0·3077	2·976
0·4891	3·879
0·0048	0·584
0·0216	0·682
0·0648	1·100
0·1311	1·736
0·2260	2·672
0·4018	3·517
$KHSO_4$ (40·00°)	
0·0109	1·745
0·0360	2·014
0·0985	3·131
0·1732	4·473
0·3077	6·466
0·4891	8·450
0·0048	1·732
0·0216	1·878
0·0648	2·592
0·1311	3·831
0·2260	5·401
0·4018	7·643

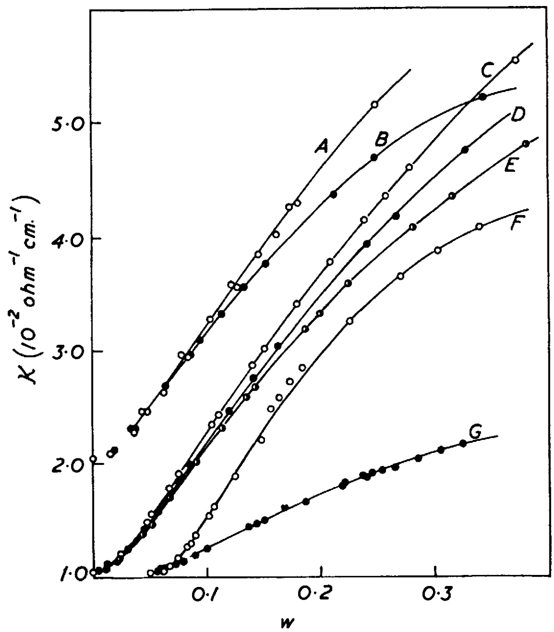
Plots of the conductivity against concentration are given in the Figure for some of the electrolytes. All the curves are of the same general shape and in the case of the metal sulphates and ketones they are initially very close to each other but diverge to an increasing amount at higher concentrations. Their initial similarity at low concentrations is a

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

consequence of the very small transport numbers of all the cations,[9] conductivities being due largely to the hydrogen sulphate ion whose conductivity is initially almost independent of the nature of the cation with which it is associated. At higher concentrations, however, the cation has a considerable effect on the mobility of the hydrogen sulphate ion and this causes the observed differences in the conductivities of different electrolytes. These differences are much too large to be attributed to the very small differences in the mobilities of the cations.

The conductivity at zero concentration is due to the ions resulting from the solvent self-dissociation and particularly the $H_3SO_4^+$ and HSO_4^- ions from the autoprotolysis. The shape of the curves at low concentrations, *i.e.*, convex to the concentration axis, is due to the repression of the autoprotolysis. At higher concentrations the curves become concave to the concentration axis, indicating that the mobility of the hydrogen sulphate ion decreases with increasing electrolyte concentration.

A, Acetone; *B*, Di-*p*-tolyl ketone: displaced vertically by 1·0 (10^{-2} ohm^{-1} cm.$^{-1}$) unit.
C, $CsHSO_4$. *D*, $KHSO_4$. *E*, $NaHSO_4$.
F, $HB(HSO_4)_4$; *G*, $H_2S_2O_7$: displaced horizontally by 0·05 *w* unit.



A more detailed consideration of the results requires a knowledge of the extent of the solvent self-dissociation at 25°. This can be obtained from the values given previously [10] for the equilibrium constants of the self-dissociation reactions at 10° and certain of the conductivity data presented above. In the following two papers these values for the equilibrium constants of the self-dissociation reactions at 25° are derived and the conductivities of electrolytes solutions that have been given in this paper are fully analysed.

Experimental

The apparatus and experimental procedures used in the measurement of conductivity have been described.[6] Sulphuric acid was prepared as described previously [2] and it was finally adjusted to exactly 100% H_2SO_4 in the conductivity cell by addition of aqueous acid or oleum until the composition of minimum conductivity [$\kappa(25°) = 0{\cdot}010432$ ohm^{-1} cm.$^{-1}$] was obtained, then by addition of the correct amount of a very dilute oleum, the 100% composition was obtained [$\kappa(25°) = 0{\cdot}010439$ ohm^{-1} cm.$^{-1}$]. It was most important to adjust the composition of the solvent accurately in this way before each run in order to obtain completely reproducible

[9] Gillespie and Wasif, *J.*, 1953, 209.
[10] Bass, Gillespie, and Robinson, *J.*, 1960, 821.

results. Powdered solid solutes were added to the conductivity cell by means of a weight-burette with a wide-bore tap and a long delivery-stem. No contamination of the contents of the cell by atmospheric moisture occurred during the short time (15 sec. or less) that the cell was open to the atmosphere.

Potassium, ammonium, lithium, and sodium sulphates were "AnalaR" materials which were dried at 120° and by storage in desiccators over phosphoric oxide. Cæsium, rubidium, silver, and thallous sulphates were the purest commercial materials obtainable and were re-crystallised from hot dilute sulphuric acid, dried at 600° for 3 hr. and stored over phosphoric oxide. Barium and strontium sulphates were prepared from the "AnalaR" nitrates by precipitation with "AnalaR" sulphuric acid and dried and stored as above. Calcium sulphate was prepared by dehydrating "AnalaR" $CaSO_4,2H_2O$ at 650°. Mercurous sulphate was precipitated from a solution of "AnalaR" mercurous nitrate with an equivalent amount of "AnalaR" sulphuric acid, washed, and dried at 250°. Lead(II) sulphate was similarly prepared from "AnalaR" lead nitrate. The purification of the ketones has been described previously.[5]

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