498. *Cryoscopic Measurements in Sulphuric Acid. Part II. The Solutes Water and Sulphur Trioxide. The Basic Strength of Water, and the Acid Strength of Disulphuric Acid.**

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The freezing point of the system water–sulphur trioxide has been studied at compositions in the neighbourhood of that of sulphuric acid. The results and conclusions differ somewhat from those of earlier investigators. From data applying to the water side of the freezing-point maximum at sulphuric acid, it is deduced that the ionisation of water as a base in solvent sulphuric acid is appreciably incomplete; a basicity constant for water is derived. From the results applying to the sulphur trioxide side of the freezing-point maximum, it is concluded that disulphuric acid * is moderately ionised; a value for its acidity constant is computed, which, however, is provisional, and is to be improved in Part IV, where account will be taken of effects, here neglected, due to the higher polysulphuric acids. From the degree of rounding of the freezing-point maximum, a value is derived for the total concentration in which solutes are formed by the self-dissociation of sulphuric acid.

(1) *Methods and Results.*

(1.1) *Objects and Background.*—Of fundamental importance for the understanding of the properties of solvent sulphuric acid is a knowledge of the behaviour of the solutes water and sulphur trioxide. The reason is partly that the study of these solutes is the first step in an investigation designed to elucidate the self-ionisation of the solvent; and it is partly that so many of the solutes, with whose condition in solvent sulphuric acid we shall be concerned in the following papers, furnish water, amongst other substances, or at least the products into which, in these conditions, water is converted.

The effect of the solutes water and sulphur trioxide on the freezing point of sulphuric acid has been investigated by Pickering (*J.*, 1890, **57**, 365), by Knietsch (*Ber.*, 1901, **34**, 4089), by Giran (*Compt. rend.*, 1913, **157**, 221), and by Hulsmann and Biltz (*Z. anorg. Chem.*, 1934, **218**, 373), but only at compositions so widely spaced that it is not possible to derive from the results any precise conclusions concerning the conditions of the solutes in dilute solution. More intensive investigations of the freezing points of dilute solutions of these solutes in sulphuric acid are recorded by Hantzsch (*Z. physikal. Chem.*, 1908, **62**, 243), by Oddo and Scandola (*Gazzetta*, 1908, **38**, 603), by Robles and Moles (*Anal. Fis. Quim.*, 1936, **34**, 331), and by Hammett and Deyrup (*J. Amer. Chem. Soc.*, 1933, **55**, 1900).

(1.2) *Method.*—A detailed reinvestigation of the freezing point of the water–sulphur trioxide system for compositions in the neighbourhood of that of pure sulphuric acid, *i.e.*, of the cryoscopic behaviour of the solutes water and sulphur trioxide in dilute solution, has now been undertaken. The results and conclusions differ somewhat from those obtained by earlier workers.

The method was to follow the change in freezing point produced by adding successive, small, weighed amounts of water to a known weight of sulphuric acid containing initially a small excess of sulphur trioxide. The freezing points were measured as is described in Part I (preceding paper). The precise amount of sulphur trioxide in the initial acid was not known at the commencement of an experiment, but after the freezing-point measurements had been made, all compositions could be calculated from the weights, with the aid of the assumption that the composition at the freezing-point maximum is that of pure sulphuric acid.

(1.3) *Results.*—The data obtained in several such experiments are given in Table I. Compositions are expressed in molalities for theoretical convenience. On the water side of the freezing-point maximum they are in molalities of water, but on the sulphur trioxide side they are given, not in molalities of sulphur trioxide, but in molalities of disulphuric acid,* the assumption having been made that the solute sulphur trioxide is converted substantially entirely in dilute solution into disulphuric acid. Of course, the distinction of composition is only that a small proportion of the total sulphuric acid counts as belonging to the solvent in one case, but not in the other; and thus the differences are numerically small, though not inappreciable.

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* The acid $H_2S_2O_7$, usually called pyrosulphuric acid, is here termed disulphuric acid, because this name belongs to a scheme of nomenclature which can conveniently be extended to the acids $H_2S_3O_{10}$ (trisulphuric acid) and $H_2S_4O_{13}$ (tetrasulphuric acid), the presence of which in oleum is cryoscopically demonstrated in Part IV of this series, and is spectroscopically confirmed in an accompanying paper (Millen); and a salt of the acid $H_2S_3O_{10}$ is described in another of the accompanying papers (Goddard, Hughes, and Ingold). The preferred nomenclature agrees with the established names of analogous acids of other elements of Group VI of the Periodic Table, *e.g.*, the polychromic, polymolybdic, and polytungstic acids.

TABLE I.

Freezing points of solutions of water and disulphuric acid in sulphuric acid.

Weights (g.).				Molality of solute.	F. p. (° c.).
Added H_2O.	Soln.	Solute.	H_2SO_4.		
Expt. No. 26 :					
		$H_2S_2O_7$.		$H_2S_2O_7$.	
—	126·07	7·084	118·99	0·3345	8·071
0·1344	126·20	5·754	120·45	0·2685	8·532
0·1311	126·33	4·458	121·87	0·2061	8·951
0·0580	126·39	3·885	122·51	0·1782	9·163
0·0751	126·47	3·144	123·33	0·1431	9·412
0·0974	126·57	2·179	124·39	0·0979	9·748
0·0654	126·64	1·533	125·11	0·0686	9·957
0·0643	126·70	0·939	125·86	0·0400	10·153
0·0315	126·73	0·628	126·10	0·0260	10·243
		H_2O.		H_2O.	
0·0635	126·79	0·0045	126·79	0·0020	10·351
0·0317	126·81	0·0362	126·79	0·0160	10·299
Expt. No. 66 :					
		$H_2S_2O_7$.		$H_2S_2O_7$.	
—	117·85	2·229	115·62	0·1048	9·694
0·0482	117·90	1·752	116·15	0·0812	9·868
0·0447	117·94	1·357	116·58	0·0598	10·015
0·0449	117·99	0·866	117·12	0·0381	10·160
0·0447	118·04	0·424	117·62	0·0168	10·289
		H_2O.		H_2O.	
0·0429	118·08	0·0074	118·07	0·0035	10·340
0·0436	118·12	0·0436	,,	0·0240	10·224
0·0445	118·17	0·0881	,,	0·0450	10·032
0·0426	118·21	0·1307	,,	0·0651	9·821
0·0450	118·25	0·1857	,,	0·0863	9·585
0·0450	118·30	0·2307	,,	0·1075	9·353
0·0439	118·34	0·2746	,,	0·1283	9·127
0·0452	118·39	0·3198	,,	0·1496	8·878
0·0469	118·44	0·3657	,,	0·1712	8·644
0·0419	118·48	0·4076	,,	0·1909	8·421
Expt. No. 67 :					
		$H_2S_2O_7$.		$H_2S_2O_7$.	
—	126·99	2·171	124·82	0·0998	9·727
0·1329	127·12	0·857	126·26	0·0401	10·144
0·0450	127·16	0·412	126·75	0·0203	10·272
0·0417	127·20	0·041	127·15	0·0020	10·350
		H_2O.		H_2O.	
0·0423	127·24	0·0378	127·20	0·0165	10·294
0·0435	127·29	0·0815	,,	0·0355	10·129
0·0452	127·33	0·1265	,,	0·0553	9·928
0·0406	127·37	0·1671	,,	0·0730	9·737
0·0400	127·41	0·2071	,,	0·0905	9·537
0·0433	127·45	0·2504	,,	0·1094	9·330
0·0433	127·49	0·3037	,,	0·1284	9·117
0·0409	127·53	0·3446	,,	0·1462	8·914
0·0426	127·57	0·3872	,,	0·1648	8·710
Expt. No. 73 :					
		$H_2S_2O_7$.		$H_2S_2O_7$.	
—	129·27	3·687	125·57	0·1650	9·248
0·1888	129·46	1·830	127·63	0·0805	9·869
0·0649	129·52	1·189	128·33	0·0521	10·064
0·0323	129·56	0·869	128·69	0·0386	10·163
0·0330	129·59	0·546	129·05	0·0238	10·253
0·0345	129·62	0·202	129·42	0·0089	10·330
		H_2O.		H_2O.	
0·0345	129·65	0·0141	129·64	0·0060	10·350
0·0344	129·68	0·0485	,,	0·0207	10·284
0·1119	129·79	0·1504	,,	0·0640	9·855
0·0645	129·85	0·2149	,,	0·0918	9·549
0·0453	129·90	0·2602	,,	0·1112	9·346
0·0670	129·97	0·3272	,,	0·1398	9·013
Expt. No. 76 :					
		$H_2S_2O_7$.		$H_2S_2O_7$.	
—	125·46	1·224	125·31	0·0553	10·066
0·0944	125·55	0·2907	125·56	0·0107	10·327
0·0294	125·58	0·0000	125·58	0·0000	10·352
		H_2O.		H_2O.	
0·0334	125·61	0·0334	125·58	0·0148	10·282
0·0339	125·64	0·0673	,,	0·0298	10·181
0·0670	125·71	0·1343	,,	0·0594	9·875
0·0592	125·79	0·1935	,,	0·0856	9·579
0·0652	125·86	0·2587	,,	0·1145	9·264
0·0644	125·92	0·3231	,,	0·1429	8·943
0·0650	125·98	0·3881	,,	0·1717	8·656
Expt. No. 79 :					
		H_2O.		H_2O.	
—	120·29	0·1150	120·18	0·0532	9·939
0·0367	120·33	0·1517	,,	0·0702	9·778
0 0692	120·40	0·2209	,,	0·1021	9·427
0·0644	120·46	0·2853	,,	0·1319	9·087
0·0682	120·53	0·3535	,,	0·1634	8·732
0·0683	120·60	0·4218	,,	0·1950	8·380
Expt. No. 80 :					
		$H_2S_2O_7$.		$H_2S_2O_7$.	
—	125·94	0·447	125·49	0·0200	10·276
0·0314	125·97	0·137	125·83	0·0061	10·337
0·0050	125·98	0·087	125·89	0·0039	10·342
		H_2O.		H_2O.	
0·0325	126·01	0·0237	125·99	0·0105	10·322
0·0327	126·04	0·0564	,,	0·0249	10·219
0·0684	126·11	0·1248	,,	0·0550	9·914
0·0663	126·17	0·1911	,,	0·0842	9·592
Expt. No. 90 :					
		H_2O.		H_2O.	
—	127·05	0·0114	127·04	0·0050	10·343
0·0345	127·08	0·0459	,,	0·0201	10·263
0·0694	127·15	0·1153	,,	0·0504	9·971
0·0686	127·22	0·1839	,,	0·0804	9·645
0·0900	127·31	0·2739	,,	0·1198	9·202
0·0739	127·38	0·3478	,,	0·1521	8·840
0·0680	127·45	0·4158	,,	0·1819	8·513
0·0700	127·52	0·4858	,,	0·2125	8·180
0·0698	127·59	0·5556	,,	0·2430	7·832
Expt. No. 102 :					
		$H_2S_2O_7$.		$H_2S_2O_7$.	
—	128·94	6·975	122·01	0·3211	8·180
0·1167	129·00	5·827	123·28	0·2654	8·563
0·2564	129·32	3·720	126·06	0·1473	9·389
0·1326	129·45	2·002	127·49	0·0882	9·809
0·1312	129·58	0·7117	128·91	0·0310	10·210
0·0677	129·65	0·0462	129·60	0·0020	10·346
		H_2O.		H_2O.	
0·0357	129·69	0·0310	129·65	0·0133	10·329
Expt. No. 103 :					
		$H_2S_2O_7$.		$H_2S_2O_7$.	
—	130·51	7·140	123·37	0·3253	8·181
0·4678	130·98	2·514	128·47	0·1100	9·668
0·1924	131·17	0·6118	130·56	0·0263	10·239
0·0307	131·20	0·3084	130·89	0·0132	10·307
		H_2O.		H_2O.	
0·0358	131·23	0·0046	131·23	0·0020	10·344

TABLE II.

Freezing points of the water–sulphur trioxide system (*Hammett and Deyrup*).

Weights (g.).				Molality	
Added H_2O.	Soln.	Solute.	H_2SO_4.	of solute.	F. p. (° c.).
Run I :					
		$H_2S_2O_7$.		$H_2S_2O_7$.	
—	53·70	2·906	50·79	0·3155	8·171
0·0737	53·77	2·228	51·54	0·2369	8·766
0·0733	53·84	1·453	52·39	0·1498	9·345
0·0595	53·90	0·884	53·02	0·0877	9·803
		H_2O.		H_2O.	
0·0874	53·99	0·0058	53·99	0·0060	10·350
0·0229	54·01	0·0287	,,	0·0296	10·180
0·0310	54·04	0·0597	,,	0·0615	9·836
0·0252	54·06	0·0849	,,	0·0874	9·532
0·0152	54·08	0·1001	,,	0·1030	9·348
0·0188	54·10	0·1189	,,	0·1224	9·127
0·0320	54·13	0·1509	,,	0·1553	8·717

Weights (g.).				Molality	
Added H_2O.	Soln.	Solute.	H_2SO_4.	of solute.	F. p. (° c.).
Run II :					
		$H_2S_2O_7$.		$H_2S_2O_7$.	
—	57·90	2·670	55·17	0·2719	8·485
0·0422	57·94	2·243	55·63	0·2265	8·810
0·0497	57·99	1·751	56·17	0·1751	9·177
0·0425	58·03	1·331	56·63	0·1321	9·482
0·0396	58·07	0·940	57·06	0·0925	9·772
0·0183	58·09	0·758	57·26	0·0744	9·905
0·0311	58·12	0·463	57·59	0·0452	10·125
0·0129	58·13	0·324	57·73	0·0315	10·220
0·0074	58·14	0·250	57·82	0·0250	10·275
0·0077	58·15	0·174	57·90	0·0164	10·315
0·0088	58·16	0·087	58·00	0·0084	10·339
		H_2O.		H_2O.	
0·0161	58·17	0·0073	58·16	0·0070	10·342
0·0158	58·19	0·0231	,,	0·0221	10·239
0·0177	58·21	0·0408	,,	0·0390	10·062
0·0941	58·30	0·1349	,,	0·1288	9·013

(1.4) *Results of Hammett and Deyrup.*—It will be necessary to compare Hammett and Deyrup's results (*loc. cit.*) for the freezing point of the water–sulphur trioxide system with those now recorded. For this purpose a recalculated version of Hammett and Deyrup's freezing-point data is presented in Table II. Here, as in Table I, compositions are expressed as molalities of water, or of disulphuric acid. Hammett and Deyrup did not record Celsius temperatures, but only readings on a Beckmann thermometer; and therefore, in order to facilitate comparison with the present results, it has been assumed that the temperature at the maximum of their freezing-point curves was 10·35° c. in every case; and all their temperature readings have been brought to this scale.

Over the range of composition with which this investigation deals, the freezing-point curve for the water–sulphur trioxide system consists of two nearly linear portions with a rounded maximum in between. This is shown in Fig. 1. ·The following discussion will largely be concerned with what can be learned from the slopes and exact shapes of the nearly linear portions, and from the amount of rounding of the maximum.

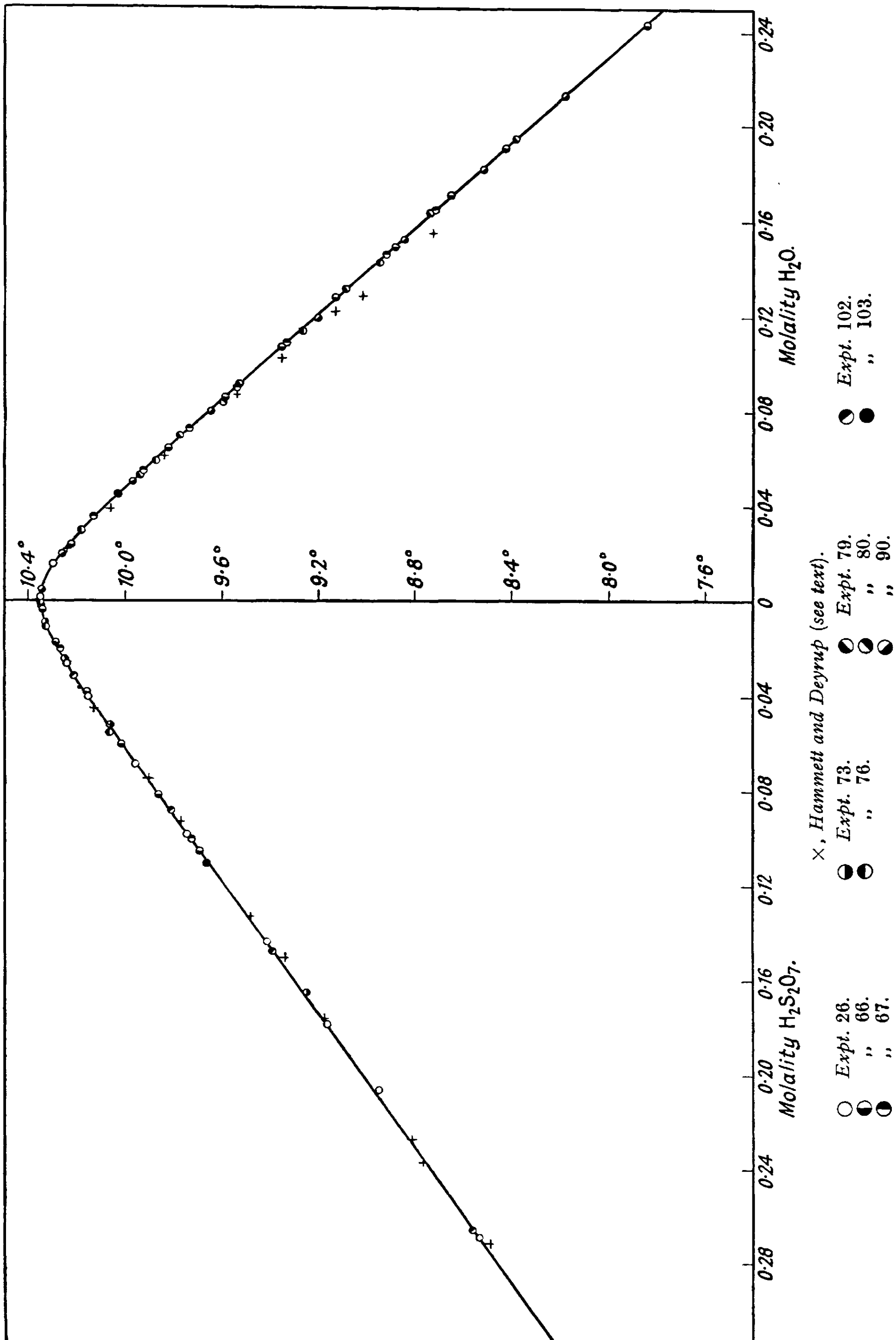
(2) *Discussion. Part I. The Solute Water.*

(2.1) *The Water Branch of the Freezing-point Curve.*—At concentrations greater than about 0·05 molal, *i.e.*, for compositions not too near those of the rounded maximum of the freezing-point curve, water behaves qualitatively like many of the solutes considered in Part I—like acetone, for instance—giving depressions of freezing point which increase nearly linearly with the solute concentration. It is therefore convenient to regard each total content of solute water as divided into two portions. One portion, of molality m_3 (about 0·05), is considered to be present for the purpose of suppressing the self-ionisation of the sulphuric acid. Its effect is to bring the freezing point from the maximum down on to the upper end of the nearly linear water-branch of the freezing-point curve, and thus to render the modified solvent suitable for study of the cryoscopic behaviour of the remainder of the water. This remainder, of molality Δm_2, now produces an additional freezing-point depression, $\Delta\theta$, down the nearly linear branch of the curve. From values of Δm_2 and $\Delta\theta$ thus defined and selected, one should be able to calculate an approximate ν-factor for water, using the theoretical formula, and the cryoscopic constant for sulphuric acid, as given in Part I.

We shall proceed on these lines, but before doing so it is necessary to note that a significant difference exists between the values now reported and those of Hammett and Deyrup: their results would make the water branch of the freezing-point curve slope more steeply than do the present measurements (cf. Fig. 1). The discrepancy is difficult to explain satisfactorily. The direction and relative magnitude of the deviations, and the slight scatter of Hammett and Deyrup's experimental points, suggest the intrusion in their experiments of a little adventitious water with each weighed water sample. Of course, such an explanation leaves a sense of doubt,

FIG. 1.

Freezing points of the system water–sulphur trioxide at compositions near that of sulphuric acid.



and therefore the present determinations of the water branch of the freezing-point curve were independently repeated a considerable number of times (more than are fully reported here) in the hope of eliminating the discrepancy. This proved impossible: the results of the experiments were so accurately consistent that one is compelled to accept them.

(2.2) *The Incomplete Ionisation of Water.*—The general nature of the conclusion to which these results lead can be seen without calculation. If we measure the average slope of the nearly linear water branch of the freezing-point curve, as determined in this investigation, we find that it is 11·21 deg. g.-mol.$^{-1}$ kg. This figure has to be compared with the cryoscopic constant of sulphuric acid, 5·98 deg. g.-mol.$^{-1}$ kg. (cf. Part I). The error which, in this simple form of comparison, arises from the lack of exact linearity of the water-branch is less than 1%. It will be evident that, if we should assume that water is completely ionised in solvent sulphuric acid according to the equation

$$H_2O + H_2SO_4 = H_3O^+ + HSO_4^-$$

then the ν-factor for water would be exactly 2, and the average slope of the water-branch would be 2 × 5·98 = 11·96 deg. g.-mol.$^{-1}$ kg., to within 1%. The observed slope falls short of this by 6%. The difference cannot be due to electrostatic activity effects, for it was shown in Part I by a comparison of non-electrolytic and electrolytic solutions (cf. *J.*, 1950, 2485 *et seq.*) that electrostatic effects are quite inappreciable in sulphuric acid solutions over the range of concentrations with which we are here concerned. The effect of solvation may not be inappreciable, but its direction is such as to widen the discrepancy. Thus it would seem necessary to conclude that water is not completely ionised in sulphuric acid.

Both Hantzsch, and Hammett and Deyrup, concluded from their cryoscopic measurements that water is almost completely ionised in sulphuric acid and they made no further comment on the matter. Hantzsch's data were, of course, not sufficiently precise to justify a consideration of somewhat small deviations. Hammett and Deyrup obtained a larger experimental slope for the water-branch of the freezing-point curve than that now found. Their slope amounted to 11·85 deg. g.-mol.$^{-1}$ kg., and, in conjunction with our cryoscopic constant, 5·98 deg. g.-mol.$^{-1}$ kg., this would mean nearly complete ionisation. But Hammett and Deyrup were using the substantially higher value, 6·15 deg. g.-mol.$^{-1}$ kg., for the cryoscopic constant, and the deviation of their measured slope from twice this value might well have suggested incomplete ionisation. However, the conclusion that water is practically completely ionised as a base in sulphuric acid was accepted by them, and seems to have been accepted quite generally.

TABLE III.

ν-Factors for solute water in solvent sulphuric acid.

Expt. no.	Molality of water. m_3.	Molality of water. Δm_2.	F. p. (° c.).	ν-Factor.
66	0·0651	—	9·821	—
	,,	0·0212	9·585	1·87
	,,	0·0424	9·353	1·81
	,,	0·0632	9·127	1·85
	,,	0·0845	8·878	1·87
	,,	0·1061	8·644	1·87
	,,	0·1258	8·421	1·87
			Mean	1·86
67	0·0730	—	9·737	—
	,,	0·0175	9·537	1·92
	,,	0·0364	9·330	1·85
	,,	0·0554	9·117	1·88
	,,	0·0732	8·914	1·89
	,,	0·0918	8·710	1·88
			Mean	1·88
76	0·0594	—	9·875	—
	,,	0·0262	9·579	1·89
	,,	0·0551	9·264	1·86
	,,	0·0836	8·943	1·88
	,,	0·1124	8·656	1·83
			Mean	1·87
79	0·0702	—	9·778	—
	,,	0·0319	9·427	1·85
	,,	0·0617	9·087	1·88
	,,	0·0932	8·732	1·88
	,,	0·1248	8·380	1·89
			Mean	1·88
90	0·0804	—	9·645	—
	,,	0·0394	9·202	1·89
	,,	0·0717	8·840	1·89
	,,	0·1015	8·513	1·88
	,,	0·1321	8·170	1·89
	,,	0·1626	7·832	1·89
			Mean	1·89

(2.3) *Approximate ν-Factors for Water.*—The average number of kinetically separate, dissolved particles (molecules or ions) which are formed in consequence of the addition of one molecule of water to the solution—the ν-factor for water—may be calculated, by the methods set forth in Part I, from observations along the nearly linear water-branch of the freezing-point curve. As a first approximation, we may employ equation (4) of Part I, substituting $s_2 = s_3 = 1$ and $\nu_2 = \nu_3 = 2$, and thus reducing the equation to the simple form written below, in which the determined value of the cryoscopic constant has been inserted :

$$\Delta\theta/\Delta m_2 = 5{\cdot}98\nu_2(1 - 0{\cdot}0035\bar{\theta}) \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

The mean depression $\bar{\theta}$ has, of course, to be reckoned with reference to the freezing point of pure sulphuric acid. Some values of ν for water, calculated in this way, are given in Table III. They lead to the mean value $\nu = 1{\cdot}89$.

The above method of calculating ν-factors is probably not the best available for two reasons. In Part I evidence was adduced for the view that potassium and ammonium hydrogen sulphates are solvated in sulphuric acid. In Part III (*J.*, 1950, paper no. 499) it will be shown that nitronium and nitrosonium hydrogen sulphates behave similarly to the potassium and ammonium salts in this respect. It seems probable that most ionic compounds, not excluding hydroxonium hydrogen sulphate, are solvated in sulphuric acid. In Section 2.6 of this paper a qualitative argument is given which suggests that the non-ionised water molecule is solvated in sulphuric acid. Confirming these assumptions, it is shown in Section 2.5 that, in the calculation of the basicity constant for water, an improvement in consistency results, if the assumption is made that both water and the ion-pair which it forms are solvated with a solvation number of about unity. The reaction of water with the sulphuric acid solvent may therefore be represented by some such equation as the following :

$$H_2O + 2H_2SO_4 = H_2O(H_2SO_4) + H_2SO_4 = H_3O(H_2SO_4)^+ + HSO_4^-$$

Accordingly, the ν-factors should be calculated by specialising equation (4) of Part I by the substitutions $s_2 = s_3 = 2$ and $\nu_2 = \nu_3 = 2$.

The conclusion that water is incompletely ionised in sulphuric acid evidently entails the consequence that the ν-factor should in principle *not* be constant and equal to 1·88 : it should rise towards 2·00 with increasing dilution. The reason why this is not apparent in Table III is that the calculations are not sufficiently accurate, and the range of water concentrations is too limited. Nevertheless theory shows that, apart from causes of curvature of which our equations take account, the nearly linear water branch of the freezing-point curve should be additionally curved, steepening from the observed slope of 11·21 deg. g.-mol.$^{-1}$ kg. to the theoretical limiting slope of 11·96 deg. g.-mol^{-1} kg. as the freezing point of pure sulphuric acid is approached. We cannot observe this because another disturbance intervenes : the slope falls to zero, owing to the self-ionisation of sulphuric acid. It will be necessary to give further consideration to this disturbance also before attempting to treat the incomplete ionisation of water more quantitatively.

(2.4) *The* (*Theoretical*) *Freezing Point of Non-dissociated Sulphuric Acid.*—It is generally accepted that the rounding of the freezing-point maximum is due to the self-ionisation of sulphuric acid. This might be a simple proton transfer :

$$2H_2SO_4 = H_3SO_4^+ + HSO_4^-$$

However, in Part IV (*J.*, 1950, paper no. 500) reasons will be given for believing that it is more complex, involving also a sulphur trioxide transfer, thus,

$$2H_2SO_4 = H_2S_2O_7 + H_2O$$

together with the ionisation of the formed disulphuric acid and water, approximately in accordance with the following equations :

$$H_2S_2O_7 + H_2SO_4 = H_3SO_4^+ + HS_2O_7^-$$
$$H_2O + H_2SO_4 = H_3O^+ + HSO_4^-$$

The hydrogen sulphate ion is a product of both forms of self-ionisation, and the hydroxonium ion is a product of the second form; wherefore the addition of water, which produces both these ions, will repress both forms of self-ionisation, and the resulting disappearance of ions will diminish the initial effect of added water in depressing the freezing point. Again, the sulphuric acidium ion arises in both forms of self-ionisation, and the hydrogen disulphate ion arises in the second form; and, since these are the ions of disulphuric acid, added sulphur trioxide will act qualitatively like added water; and thus we should find rounding on both sides of the freezing-point maximum, as, indeed, we do.

In order to be able to compute the degree of ionisation of water as a function of its concentration, we require to know what the freezing point of sulphuric acid would be in the absence of any self-ionisation. This temperature cannot be estimated by merely producing backwards the nearly linear branches of the freezing-point curve, so that they meet in a point above the rounded maximum; for, as we have seen in the case of the water branch—and a quite similar argument applies to the sulphur trioxide branch—these nearly linear branches are not linear; in particular, they would steepen materially, if it were not for the disturbances of self-ionisation, at compositions close to that of sulphuric acid. Therefore it is necessary to find, by trial calculations, that value of the theoretical freezing point which gives the most consistent results on applying it to the computation of the degree of ionisation of water. The value finally chosen, 10·62°, is probably not in error by more than 0·02°.*

(2.5) *The Basic Strength of Water in Sulphuric Acid.*—By calculating freezing-point depressions as differences between the theoretical freezing point of non-dissociated sulphuric acid and the observed freezing points of solutions of water in sulphuric acid, over the solute concentration range 0·05—0·25 molal, it is possible to compute the equilibrium constant

$$K_b(H_2O) = [H_3O^+][HSO_4^-]/[H_2O]$$

Two steps are involved. Writing $\Delta\theta'$ for the freezing-point depression calculated from the theoretical freezing point, and $\Delta m = m_3 + \Delta m_2$ for the *total* molality of solute water, a ν-factor is first computed from the equation

$$\Delta\theta'/\Delta m = 5{\cdot}98\,\nu\,(1 + 0{\cdot}0035\,\bar{\theta}') \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

(cf. equation 1, p. 2498). Here $\bar{\theta}'$ is to be obtained by subtracting, from the real freezing point of sulphuric acid, 10·36°, the mean between the freezing point of the solution and the theoretical freezing point of non-dissociated sulphuric acid, 10·62°. Having thus found ν, the basic ionisation constant is computed from the mass-law equation

$$K_b(H_2O) = (\nu - 1)^2 m/(2 - \nu) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

This procedure neglects two disturbances. The first arises from incompleteness in the suppression, by the added water, of the self-dissociation of the solvent. This can be computed from the values, given in Part IV, of the equilibrium constants of the two main dissociation processes of sulphuric acid, *viz.*,

$$2H_2SO_4 \rightleftharpoons H_3SO_4^+ + HSO_4^-$$
$$K_{ap} = [H_3SO_4^+][HSO_4^-] = 1{\cdot}7 \times 10^{-4}\text{ g.-mol.}^2\text{ kg.}^{-2}$$
$$2H_2SO_4 \rightleftharpoons H_3O^+ + HS_2O_7^-$$
$$K_{id} = [H_3O^+][HS_2O_7^-] = 0{\cdot}7 \times 10^{-4}\text{ g.-mol.}^2\text{ kg.}^{-2}$$

In calculating the residual self-dissociation, we take the added water as completely converted into H_3O^+ and HSO_4^-. Having from the above constants computed $[H_3SO_4^+]$ and $[HS_2O_7^-]$, we employ the formula $\delta\theta = 11{\cdot}96([H_3SO_4^+] + [HS_2O_7^-])$, which gives, with sufficient approximation, the freezing-point depression $\delta\theta$ due to the surviving self-dissociation. This must be subtracted from $\Delta\theta'$ to give $\Delta\theta'' = \Delta\theta' - \delta\theta$.

There remains the disturbance caused by solvation. In order to take it into account, it is necessary to calculate ν-factors, neither with equation (2), nor with this equation with $\Delta\theta''$ written for $\Delta\theta'$, but by means of an equation for $\Delta\theta''/\Delta m$, which is derived from equation (4) of Part I by writing $s_2 = s_3 = n + 1$ and $\nu_2 = \nu_3 = 2$ in the nearly unit correction factor. Here n is the solvation number of hydroxonium hydrogen sulphate. The equation is

$$\Delta\theta''/\Delta m = 5{\cdot}98\nu\,(1 - 0{\cdot}0035\bar{\theta}' + 2n\bar{m}/10{\cdot}20) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

and the ν-factors derived from it have to be inserted into equation (3) for the purpose of computing $K_b(H_2O)$.

The method employed for the evaluation of the solvation number n is so to choose it that the most nearly constant values of K_b result. Unfortunately, there is a large percentage error in the determination of K_b, because, as equation (3) shows, the value derived depends fundamentally on the small quantity $2 - \nu$, that is, on the experimental determination of the small difference between the actual slope of the water branch of the freezing-point curve and the slope it would have if the ionisation of water were as complete as has hitherto been thought. For this reason the solvation number cannot be determined at all exactly. However, the

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* The freezing point, 10·62°, in the absence of all forms of dissociation, is to be distinguished from the freezing-point, 10·52°, in the absence only of the autoprotolysis (cf. Part I, *J.*, 1950, 2488).

calculations have been made with various trial values, $n = 0, 1, 2$, etc., and $n = 1$, which gives moderately consistent K_b values, has been selected as the best round figure.

The upper part of Table IV contains two of the sets of K_b values which have been computed for experiment No. 90. One set (headed $n = 0$) is derived by neglecting solvation. The other (headed $n = 1$) is computed with the inclusion of a correction for solvation, the solvation number being taken as unity. The lower part of Table IV contains a summary of the mean K_b values calculated from all the experiments, with the same allowance for solvation. From the overall mean, $K_b = 1{\cdot}2$ g.-mol. kg.$^{-1}$, it can be computed that, at 0·1 molal concentration, about 7% of water remains non-ionised in solvent sulphuric acid.

TABLE IV.

Basic ionisation constant of water in sulphuric acid (*Expt.* 90).

Molality, H_2O (m).	F. p. (° c.).	Depression. $\Delta\theta'$.	$\Delta\theta''$.	ν-Factors. $n = 0$.	$n = 1$.	$K_b(H_2O)$. $n = 0$.	$n = 1$.
0·0504	9·971	0·649°	0·596°	1·98	1·97	—	—
0·0804	9·645	0·975	0·940	1·96	1·94	1·9	1·2
0·1198	9·202	1·418	1·395	1·95	1·93	2·2	1·5
0·1521	8·840	1·780	1·758	1·94	1·91	2·2	1·5
0·1819	8·513	2·147	2·089	1·93	1·90	2·3	1·5
0·2125	8·170	2·450	2·436	1·93	1·89	2·6	1·5
0·2430	7·872	2·788	2·777	1·92	1·87	2·6	1·5

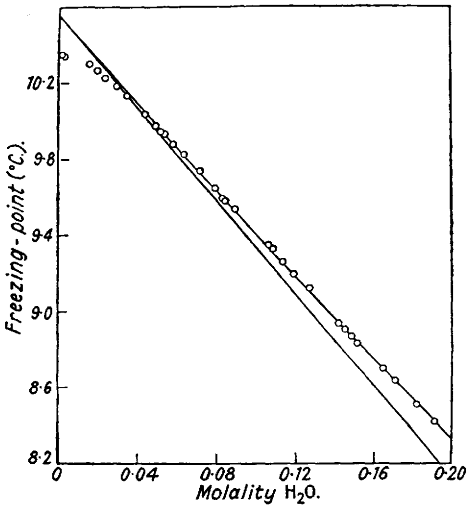
Summary of basicity constants (calc. with $n = 1$) :

Expt. No.	66	67	76	79	90	Mean
$K_b(H_2O)$	1·1	1·1	1·3	1·1	1·4	1·2 g.-mol. kg.$^{-1}$.

The value of K_b is somewhat uncertain, because it is very sensitive to the error of experiment and of the applied corrections. If we neglect solvation, the mean value of K_b becomes 1·8 g.-mol. kg.$^{-1}$. If we retain the correction for solvation, but neglect the residual solvent dissociation, then the derived value is 0·72 g.-mol. kg.$^{-1}$. For the purpose of reproducing experimental results by calculation, it matters little which value is taken provided the computing procedure corresponds to the value assumed. In Fig. 2 a theoretical freezing-point curve for water is shown, which is computed from the last-mentioned value; and it is compared with the experimental points. The upper part of the diagram shows the effect on the freezing point of the repression by the added water of the self-ionisation of sulphuric acid. The lower curve is calculated from equation (3) by taking ν as constant and equal to 2.

FIG. 2.

Theoretical freezing-point curves for solute water in solvent sulphuric acid.



(2.6) *Remarks on the Basicity of Water in Sulphuric Acid.*—The conclusion that water is incompletely ionised in sulphuric acid whilst, as was shown in Part I, acetic acid and acetone are fully ionised in this solvent, seems to invite comment. When water, acetic acid, and acetone are acting as solvents for acids, *e.g.*, for the hydrogen halides, water is definitely more basic than either acetic acid or acetone. Yet when these three substances have the role of solutes in solvent sulphuric acid, water is less basic than either of the other two. This illustrates the recognised impossibility of setting up an absolute table of acid-strengths or base-strengths; and it shows that specific molecular interactions between solute and solvent play a part, which can be at least as important as are differences of proton affinity, in the determination of acid–base equilibria.

As to the reason for the small basicity of water in sulphuric acid, the obvious line of thought is that the relatively considerable thermodynamic stability of non-ionised water in solvent sulphuric acid is to be ascribed to solvation; and, more particularly, to the ability of a water molecule to occupy the place of a sulphuric acid molecule in the closely-knit hydrogen-bonded structure of liquid sulphuric acid (cf. Part I), and to do this without disrupting the surrounding liquid structure. The non-ionised forms of the solutes acetone and acetic acid will, because of the size of these molecules, and the lack of affinity of their hydrocarbon portions for sulphuric acid, cause a considerable disruption of the surrounding sulphuric acid structure. They will be rendered by this much less stable relatively to their ionised forms.

(3) *Discussion. Part II. The Solute Sulphur Trioxide.*

(3.1) *The Sulphur Trioxide Branch of the Freezing-point Curve.*—The general form of this branch of the freezing-point curve will be clear from Fig. 1: at compositions sufficiently removed from the rounded maximum, the sulphur trioxide branch becomes nearly linear, but much less sloping than the water branch. The mean slope, according to the present determinations, for a range of concentrations of disulphuric acid from 0·3 molal to 0·05 molal, is 7·40 deg. g.-mol.$^{-1}$ kg. Obviously disulphuric acid is yielding many fewer ions than water produces.

Hantzsch concluded from his cryoscopic measurements that disulphuric acid was almost completely non-ionised in sulphuric acid. He found, however, that these dilute oleum solutions have quite a high electrical conductivity. He therefore assumed that disulphuric acid is a very weak acid, but that the hydrogen ion in sulphuric acid possesses an unusually high mobility.

Hammett and Deyrup record the value 7·55 deg. g.-mol.$^{-1}$ kg. for the slope of the nearly linear part of the sulphur trioxide branch of the freezing-point curve. Their conclusion was either that disulphuric acid was a weak electrolyte, or that it undergoes a complex ionisation involving the polymerisation of sulphur trioxide.

The simplest explanation of the fact that sulphur trioxide gives a curve of freezing-point depressions having a slope intermediate between those appropriate to a non-electrolyte and a binary electrolyte is that, in dilute solution in sulphuric acid, solute sulphur trioxide is converted almost completely into disulphuric acid, which is ionised as a weak acid according to the equation:

$$H_2S_2O_7 + H_2SO_4 = H_3SO_4^+ + HS_2O_7^-$$

Actually this assumption is too simple. For it will be shown in Part IV (*J.*, 1950, paper no. 500) that solutions of sulphur trioxide in sulphuric acid contain, besides disulphuric acid, appreciable amounts of higher polysulphuric acids. However, for the present we shall, for simplicity, neglect the disturbance caused by these higher acids, although the estimates which we shall thus derive of the degree of ionisation of disulphuric acid will be only provisional and will be shown in Part IV to require a significant correction.

It should be remarked that the conclusion that sulphur trioxide is converted in dilute solution mainly into disulphuric acid does not follow from the cryoscopic results; as far as they are concerned, the distinction between sulphur trioxide and non-ionised disulphuric acid molecules is only slight, one being merely a monosolvated form of the other. But the fact that, on increasing the concentration of sulphur trioxide until a new solid phase appears, the new phase is, not sulphur trioxide, but disulphuric acid, shows that, even in such relatively high concentration, solute sulphur trioxide is converted largely into disulphuric acid; and it is a fair assumption that this conversion will be much more nearly complete in the dilute solutions relevant to this work. In principle, the cryoscopic results will measure (*a*) the concentration of the ions of disulphuric acid, and (*b*) the concentration of the non-ionised disulphuric acid molecules *plus* any free sulphur trioxide. The concentration of free sulphur trioxide is expected to bear a small constant proportion to the concentration of non-ionised molecules of disulphuric acid. It is difficult to say whether or not this small proportion is completely negligible, but if it is not, then these small concentrations of sulphur trioxide must be held to be included in the stated concentrations of non-ionised disulphuric acid.

(3.2) *The Acid Strength of Disulphuric Acid in Solvent Sulphuric Acid.*—It has been mentioned that the average slope of the nearly linear part of the sulphur trioxide branch of the freezing-point curve is 7·40 deg. g.-mol.$^{-1}$ kg. But, as already illustrated in the example of the solute water, this figure has no simple and exact molecular significance; for not only is the nearly linear curve in fact non-linear, but also it is theoretically expected to be non-linear for various reasons, of which the most important relates to the different proportions in which disulphuric acid should be ionised at different dilutions, according to Ostwald's law. This effect should cause the curve to steepen, from slopes in the neighbourhood of 7·40 deg. g.-mol.$^{-1}$ kg. to a limiting slope of 11·96 deg. g.-mol.$^{-1}$ kg., as the composition of pure sulphuric acid is approached. One does not observe this, because the self-ionisation of the solvent causes the gradient actually to fall away at compositions near that of sulphuric acid. Indeed, over a considerable band of concentrations, the two effects, one tending to steepen the curve and the other tending to slacken its gradient, nearly cancel each other, producing a deceptive near-linearity and a slope which is meaningless from a molecular point of view.

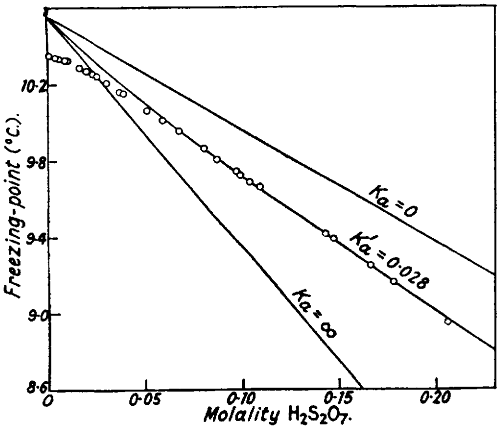
The procedure for calculating ν, and hence the equilibrium constant

$$K_a(H_2S_2O_7) = [H_3SO_4^+][HS_2O_7^-]/[H_2S_2O_7]$$

is similar to that illustrated for the solute water. Using the theoretical freezing point of the non-dissociated solvent, we compute ν, as a function of concentration, by means of an appropriate form of the general equation, employing for the purpose observations of freezing point in the region of concentration 0·08—0·35 molal disulphuric acid. The equation used is derived from equation (4) of Part I by inserting the approximate figure $\nu_2 = 1·3$ into the nearly unit correction factor, and by substituting also $s_2 = \nu_2 - 1 = 0·3$, as is required for the reaction

FIG. 3.

Theoretical freezing-point curves for the solute disulphuric acid in solvent sulphuric acid.



$$H_2S_2O_7 + H_2SO_4 = H_3SO_4^+ + HS_2O_7^-$$

(since $m_3 = 0$, values for s_3 and ν_3 are not required). The resulting equation is

$$\Delta\theta'/\Delta m = 5·98\nu\,(1 - 0·0035\bar{\theta}' - 0·7\bar{m}/10·20) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where Δm is the total molarity of disulphuric acid, $\Delta\theta'$ is the depression of freezing point, reckoned with reference to the theoretical freezing point, $\bar{m}$ is the mean molality over the finite interval, and $\bar{\theta}'$ is the mean depression computed as stated on p. 2499. The ν-factors thus obtained are now improved as follows. From them, the approximate concentrations $[H_3SO_4^+]$ and $[HS_2O_7^-]$ are derived. From these, and the already mentioned ionic products K_{ap} and K_{id}, we compute the small concentrations of surviving HSO_4^- and H O.$^+$ and thence the partial depressions, $\delta\theta = 11{\cdot}96([HSO_4^-] + [H_3O^+])$, caused by residual self-dissociation. These partial depressions are now applied as corrections, $\Delta\theta'' = \Delta\theta' - \delta\theta$, and equation (5) is used again, but with $\Delta\theta''$ replacing $\Delta\theta'$. The final step is to compute the equilibrium constant $K_a(H_2S_2O_7)$ by means of the mass-law equation

$$K_a(H_2S_2O_7) = (\nu - 1)^2 m/(2 - \nu) \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (6)$$

Some values of K_a, thus deduced from two experiments, are given in Table V.

TABLE V.

Acid ionisation constant of disulphuric acid in sulphuric acid.

Molality of $H_2S_2O_7$.	F. p. (° c.).	Depression. $\Delta\theta'$.	$\Delta\theta''$.	ν ($n = 0$).	$K_a(H_2S_2O_7)$.
Expt. No. 26 :					
0·0979	9·748	0·872°	0·802°	1·38	0·023
0·1431	9·412	1·210	1·158	1·36	0·029
0·1782	9·163	1·457	1·411	1·34	0·031
0·2061	8·951	1·669	1·627	1·33	0·033
0·2685	8·532	2·088	2·052	1·30	0·035
0·3345	8·071	2·549	2·519	1·28	0·036
Expt. No. 102 :					
0·0882	9·809	0·811	0·743	1·42	0·027
0·1473	9·389	1·231	1·177	1·35	0·028
0·2054	8·563	2·057	2·019	1·29	0·031
0·3211	8·180	2·440	2·406	1·27	0·032

From these figures, and similar computations based on other experiments, one may deduce a mean value of the acid dissociation constant of disulphuric acid in sulphuric acid, *viz.*, $K_a(H_2S_2O_7) = 0{\cdot}028$ g.-mol. kg.$^{-1}$. Disulphuric acid in sulphuric acid is thus a *somewhat* weak acid (like oxalic acid in water).

Using the above value, a theoretical freezing-point curve for the solute sulphur trioxide has been constructed, just as was done for the solute water. This curve (labelled $K_a' = 0{\cdot}028$) is compared with the experimental data in Fig. 3. The other curves in Fig. 3 (labelled $K_a = 0$ and $K_a = \infty$) are the theoretical curves for disulphuric acid, considered as a non-electrolyte and as a strong electrolyte, *i.e.*, they are the curves for which ν has the values 1 and 2, respectively.

The value 0·028 g.-mol. kg.$^{-1}$ here derived for the acid dissociation constant of disulphuric acid in sulphuric acid will be termed the *apparent* dissociation constant of disulphuric acid, and it will be designated $K_a'(H_2S_2O_7)$, as is done in Fig. 3. This is because the value has been computed without making an allowance (for which we have as yet no method) for the formation and ionisation of the higher polysulphuric acids. It will be shown in Part IV that the effect of the formation of these higher poly-acids is not negligible, and that, on this account, the apparent acidity constant of disulphuric acid is substantially larger than the true value.

(4) *Discussion. Part III. Self-dissociation of Sulphuric Acid.*

An important datum for the study of the dissociation of sulphuric acid follows from the results reported here. This datum is the total concentration of all the solute species which arise by the self-dissociation of pure sulphuric acid. Its value may be obtained from the difference between the calculated freezing-point of undissociated sulphuric acid and the maximum observed freezing-point of real sulphuric acid. The difference is 10·62° − 10·36° = 0·26°, and it corresponds to the total solute concentration 0·043 molal. Assuming the dissociation products to be entirely ionic, the total concentration of uni-univalent electrolytes is thus 0·0215 molal. The problem of the determination of the individual products of the self-dissociation is considered further in Part IV.

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