378. *Solutions in Sulphuric Acid. Part XIX.* The Formation of Tetra(hydrogen sulphato)boric Acid and its Anion in Solutions of Boric Acid and Boric Oxide.*

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It is shown by means of cryoscopic and conductivity measurements on boric oxide and boric acid solutions in sulphuric acid that the boron tetra(hydrogen sulphate) ion $B(HSO_4)_4^-$ is formed according to the equations

$$B_2O_3 + 9H_2SO_4 = 2B(HSO_4)_4^- + 3H_3O^+ + HSO_4^-$$
$$H_3BO_3 + 6H_2SO_4 = B(HSO_4)_4^- + 3H_3O^+ + 2HSO_4^-$$

The 1050-cm.$^{-1}$ line of the hydrogen sulphate ion has been found in the Raman spectrum of solutions of boric acid in sulphuric acid. By dissolving boric acid or boric oxide in oleum, solutions can be obtained of tetra(hydrogen sulphato)boric acid, $H[B(HSO_4)_4]$, which is a strong acid, so far the only known strong acid of the sulphuric acid solvent system: $H[B(HSO_4)_4] + H_2SO_4 = H_3SO_4^+ + B(HSO_4)_4^-$. This acid can be titrated cryometrically and conductometrically with a strong base such as potassium hydrogen sulphate:

$$\underset{\text{acid}}{H[B(HSO_4)_4]} + \underset{\text{base}}{KHSO_4} = \underset{\text{salt}}{K[B(HSO_4)_4]} + \underset{\text{solvent}}{H_2SO_4}$$

This is a typical acid–base neutralisation reaction in the sulphuric acid solvent system.

Various compounds have been reported as the products of reactions of boric acid and boric oxide with sulphuric acid, oleum, or sulphur trioxide. Thus Merz [1] stated that a substance having a composition corresponding to $5B_2O_3,2SO_3,2H_2O$ could be obtained by heating boric acid with concentrated sulphuric acid and volatilising the excess of sulphuric acid at 260°. By dissolving boric oxide in oleum, Schultz and Sellac [2] claimed to have obtained crystals of the composition $B_2O_3,3SO_3,H_2O$, and from the reaction between boric acid and sulphur trioxide d'Arcy [3] obtained a white solid of composition $H_3BO_3,3SO_3$ or $B(HSO_4)_3$. By heating boric oxide and sulphur trioxide in a sealed tube at 115° Pictet and Karl [4] obtained a compound B_2O_3,SO_3, and at 250° a compound $B_2O_3,2SO_3$. Hantzsch [5] measured the freezing-point depression produced by boric oxide in sulphuric acid and obtained van't Hoff i factors of approximately 6—8 which he interpreted as being due to the reaction

$$B_2O_3 + 9H_2SO_4 = 2B(HSO_4)_3 + 3H_3O^+ + 3HSO_4^-$$

We have investigated the reaction that occurs when boric acid or boric oxide is dissolved in a large excess of 100% sulphuric acid or dilute oleum by measuring the freezing points and electrical conductivities of the solutions thus formed.

Experimental

Apparatus.—The apparatus and general procedure for making the cryoscopic measurements were described in Part I.[6] Freezing points were measured either with a platinum-resistance thermometer and a Smith's difference bridge as described in Part I, or with a solid-stem mercury-in-glass thermometer which was periodically calibrated against the platinum-resistance thermometer.[7]

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* Part XVIII, *J.*, 1956, 80.

[1] Merz, *J. prakt. Chem.*, 1866, **99**, 179.

[2] Schultz and Sellac, *Ber.*, 1871, **4**, 15.

[3] d'Arcy, *J.*, 1889, **55**, 159.

[4] Pictet and Karl, *Bull. Soc. chim. France*, 1908, **3**, 114.

[5] Hantzsch, *Z. phys. Chem.*, 1908, **61**, 257.

[6] Gillespie, Hughes, and Ingold, *J.*, 1950, 2473.

[7] Gillespie and Leisten, *J.*, 1954, 1.

The apparatus used for making the conductivity measurements was an improved form of that used by Gillespie and Wasif[8] and will be fully described in a later paper.[9]

Materials.—Sulphuric acid and oleum were prepared as described by Gillespie and Oubridge.[10] " AnalaR " boric acid was dried for several days in a desiccator over phosphoric oxide.

Boric oxide was prepared by controlled dehydration of " AnalaR " boric acid under vacuum. The boric acid was heated in a Pyrex tube which was gradually raised to 280° during several hours and kept at this temperature for 24 hr. under vacuum with continual pumping.[11] The boric oxide was manipulated in a dry-box and stored in a desiccator over phosphoric oxide. It was estimated by titration against standard sodium hydroxide solution in the presence of excess of mannitol. The sample used was 98·5% B_2O_3, the impurity presumably being water.

Calculation of Results.—The freezing-point depression θ is related to the molality of the solute m_2 by the equation

$$\theta/m_2 = 6{\cdot}12\nu_2 g(1 - 0{\cdot}00195\theta)[1 + (2s_2 - \nu_2)m_2/2m_1] \quad . \quad . \quad . \quad . \quad . \quad (1)$$

which is equation (2) of Part XVII[10] where ν_2 is the number of moles of ions and molecules formed from one mole of the solute, and the other symbols have the meanings given in Part XVII. The value of g for solutions of univalent electrolytes generally lies between 0·95 and 1·05 in the range of composition with which we are concerned. Thus, to determine ν_2 approximately in order to distinguish between different modes of ionisation, we may reasonably set $g = 1$ and write equation (1) in the form

$$\theta/m_2 = 6{\cdot}12\nu'(1 - 0{\cdot}00195\theta)[1 + (2s_2 - \nu')m_2/2m_1] \quad . \quad . \quad . \quad . \quad (2)$$

where we have replaced ν_2 by ν' to indicate that it is an approximate value only ($\nu' = \nu_2 g$).

The freezing-point depressions θ were calculated from the hypothetical freezing point ($T_0'' = 10{\cdot}580°$) of completely undissociated sulphuric acid, and the observed freezing points were corrected to allow for the incomplete repression of the self-ionisation equilibria by means of the equilibrium constants[6,10] $K_{ap} = 1{\cdot}56 \times 10^{-4}$ and $K_{id} = 2{\cdot}8 \times 10^{-5}$. The values of T_0'' and K_{id} are revised values differing slightly from those quoted in Part XVII. They will be more fully discussed in a later paper.

A supercooling correction of $\delta T = 0{\cdot}0125s\theta'$, where s is the amount of supercooling and θ' is the freezing-point depression calculated from 10·365°, was applied to all the observed freezing points.[6,10]

RESULTS AND DISCUSSION

Cryoscopic Measurements on Boric Acid and Boric Oxide in 100% Sulphuric Acid.—Table 1 shows that both boric acid and boric oxide give values of ν' of approximately 6 in 100% sulphuric acid. From a consideration of the earlier work of d'Arcy[3] and Hantzsch[5] the most probable reaction would appear to be the formation of boron tri(hydrogen sulphate):

$$H_3BO_3 + 3H_2SO_4 = B(HSO_4)_3 + 3H_2O \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

which, since the water formed is ionised in sulphuric acid, may be written

$$H_3BO_3 + 6H_2SO_4 = B(HSO_4)_3 + 3H_3O^+ + 3HSO_4^- \quad . \quad . \quad . \quad . \quad (2)$$

and for boric oxide

$$B_2O_3 + 9H_2SO_4 = 2B(HSO_4)_3 + 3H_3O^+ + 3HSO_4^- \quad . \quad . \quad . \quad (3)$$

These reactions correspond to ν' values of 7 and 8 respectively, which is not in agreement with the experimental observations. The discrepancy is, however, removed in both cases if it is assumed that boron tri(hydrogen sulphate) reacts further with a hydrogen sulphate ion to form the boron tetra(hydrogen sulphate) ion

$$B(HSO_4)_3 + HSO_4^- = B(HSO_4)_4^- \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

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[8] Gillespie and Wasif, *J.*, 1953, 204.

[9] Gillespie and Solomons, to be published.

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

[11] *Inorg. Synth.*, 1946, **2**, 22.

TABLE 1. *Freezing points of solutions of boric acid and boric oxide in sulphuric acid.*

m_2	F. p., obs.	F. p., corr.	θ	ν'	m_2	F. p., obs.	F. p., corr.	θ	ν'
				Boric acid.					
				Expt. 139					
—	10·365°	10·580°	—	—	0·03112	9·422°	9·454°	1·126°	5·87
0·00560	10·257	10·374	0·206°	6·01	0·03704	9·220	9·248	1·332	5·81
0·01426	9·993	10·057	0·523	5·98	0·05059	8·750	8·770	1·810	5·78
0·02056	9·783	9·831	0·749	5·93	0·06859	8·116	8·131	2·449	5·74
0·02465	9·642	9·682	0·898	5·93					
				Expt. 111.					
—	10·363	10·580	—	—	0·04391	8·971	8·995	1·585	5·84
0·00948	10·129	10·217	0·363	6·10	0·05541	8·576	8·595	1·985	5·78
0·02241	9·710	9·755	0·825	5·98	0·06958	8·098	8·113	2·467	5·69
0·03213	9·374	9·405	1·175	5·93					
				Expt. 108.					
—	10·365	10·580	—	—	0·06331	8·332	8·348	2·232	5·67
0·03909	9·154	9·183	1·397	5·78	0·07193	8·038	8·053	2·527	5·65
0·04991	8·785	8·806	1·774	5·74					
				Boric oxide.					
				Expt. 119.					
—	10·361	10·580	—	—	0·04574	8·832	8·873	1·707	5·99
0·02131	9·695	9·770	0·810	6·13	0·05704	8·438	8·472	2·108	5·91
0·03601	9·189	9·240	1·340	6·00	0·06669	8·121	8·149	2·431	5·81

which is analogous to BF_4^- and the borate ion[12] $B(OH)_4^-$. The complete equations then become

$$H_3BO_3 + 6H_2SO_4 = B(HSO_4)_4^- + 3H_3O^+ + 2HSO_4^- \quad . \quad . \quad . \quad (5)$$

$$B_2O_3 + 9H_2SO_4 = 2B(HSO_4)_4^- + 3H_3O^+ + HSO_4^- \quad . \quad . \quad . \quad (6)$$

from which it may be seen that both boric acid and boric oxide should have ν' values of approximately 6, as observed. The fact that the ν' decreases with increasing concentration to somewhat below 6 is consistent with the formation of water as one product of these reactions, since water has a ν' value of somewhat less than 2 which decreases with increasing concentration.[13] The cryoscopic results are therefore consistent with these ionisations for boric acid and boric oxide, but they do not necessarily prove that they are correct. It is, however, difficult to think of reasonable alternative modes of ionisation that also give ν' values of 6. One possible alternative can be formulated by analogy with the ionisation of nitric acid, $HNO_3 + 2H_2SO_4 = NO_2^+ + H_3O^+ + 2HSO_4^-$, namely

$$H_3BO_3 + 3H_2SO_4 = BO^+ + 2H_3O^+ + 3HSO_4^- \quad . \quad . \quad . \quad . \quad (7)$$

$$B_2O_3 + 3H_2SO_4 = 2BO^+ + H_3O^+ + 3HSO_4^- \quad . \quad . \quad . \quad . \quad . \quad (8)$$

Conductivity Measurements on Boric Acid and Boric Oxide in 100% *Sulphuric Acid*.—Fortunately we can readily distinguish between the type of ionisation represented by equations (5) and (6) and that represented by equations (7) and (8) by means of conductivity measurements. Because of the occurrence of chain conduction the mobilities of the hydrogen sulphate ion (HSO_4^-) and the hydrogen ion ($H_3SO_4^+$) are very much greater than those of other ions;[14] hence the conductivity of a solution of a basic electrolyte is determined almost entirely by the hydrogen sulphate ions, and that of an acidic electrolyte by the hydrogen ions ($H_3SO_4^+$). Thus from the observed conductivities of an electrolyte the number of moles of hydrogen sulphate ion or hydrogen ion produced by one mole of the electrolyte may readily be determined. Equation (5) shows that boric acid should behave

[12] Edwards, Morrison, Ross, and Schultz, *J. Amer. Chem. Soc.*, 1955, **77**, 266.

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

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

as a di(hydrogen sulphate), and equation (6) that boric oxide should behave as a mono(hydrogen sulphate), whereas if ionisation occurs as in equations (7) and (8) both boric acid and boric oxide should behave as tri(hydrogen sulphates).

TABLE 2. *Specific conductances of solutions of boric acid and boric oxide in sulphuric acid.**

c (M) *	100κ	c (M) *	100κ	c (M) *	100κ	c (M) *	100κ	c (M) *	100κ	c (M) *	100κ
Boric acid.											
Expt. 1.								Expt. 2.			
0·0000	1·043	0·0381	1·354	0·0812	1·979	0·0000	1·043	0·0272	1·218	0·0590	1·659
0·0062	1·050	0·0504	1·530	0·1052	2·311	0·0038	1·049	0·0418	1·410	0·0818	1·994
0·0146	1·091	0·0613	1·691	0·1369	2·716	0·0118	1·076				
0·0256	1·195	0·0695	1·809	0·1749	3·148						
Boric oxide.											
Expt. 4.								Expt. 12.			
0·0000	1·043	0·0592	1·260	0·1043	1·542	0·0000	1·043	0·0395	1·137	0·1509	1·776
0·0382	1·142	0·0839	1·412	0·1613	1·873	0·0081	1·045	0·0678	1·285	0·1795	1·925
						0·0168	1·058	0·1052	1·510		

* Molarities given in this and the following tables have been calculated by assuming that the densities of the solutions are the same as that of the solvent.

The results of the conductivity measurements are given in Table 2 and in Fig. 1. the observed specific conductances are compared with those of solutions of water.[14,9] It may be seen that boric acid solutions have conductivities very similar to those of solutions of water of twice the concentration, and that boric oxide solutions have conductivities that are very similar to solutions of water of the same concentration as would be expected if they ionise according to equations (5) and (6). Molar conductances for boric oxide and boric acid are compared with those for some other electrolytes in Tables 3 and 4. Again,

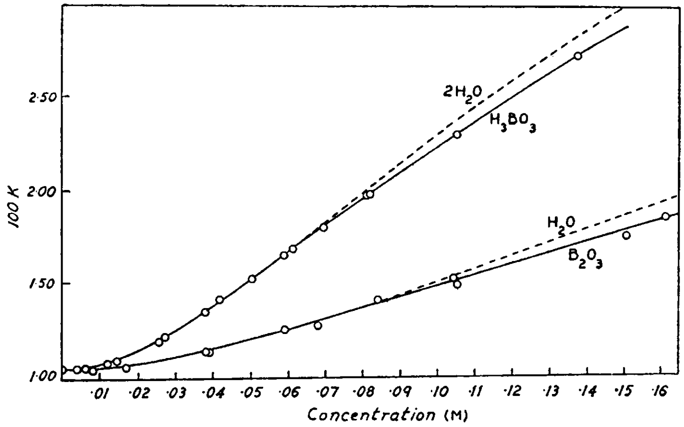

FIG. 1. *Specific conductances of solutions of boric acid and boric oxide in sulphuric acid.*

TABLE 3. *Comparison of the molar conductances of boric acid and some di(hydrogen sulphates).*

c (M)	H_3BO_3	$2H_2O$	HNO_3	$Ba(HSO_4)_2$	c (M)	H_3BO_3	$2H_2O$	HNO_3	$Ba(HSO_4)_2$
0·05	306	304	306	304	0·15	191	200	197	179
0·10	224	231	229	221	0·20	169	181	177	150

TABLE 4. *A comparison of the molar conductances of boric oxide and some mono(hydrogen sulphates).*

c (M)	B_2O_3	H_2O	$KHSO_4$	c (M)	B_2O_3	H_2O	$KHSO_4$	c (M)	B_2O_3	H_2O	$KHSO_4$
0·05	240	236	241	0·10	152	152	151	0·15	124	128	127

we see clearly that boric acid behaves as a di(hydrogen sulphate) and boric oxide as a mono(hydrogen sulphate). The conductivity measurements thus show unambiguously that ionisation does not occur according to equations (7) and (8), and they provide additional strong support for ionisation according to equations (5) and (6). Indeed, we have not been able to formulate any alternative modes of ionisation which satisfy all the conditions imposed by the results of the cryoscopic and conductivity measurements.* Further evidence in support of the ionisations represented by equations (5) and (6) has been obtained from cryoscopic and conductometric measurements in oleum solutions.

Cryoscopic Measurements in Oleum Solutions.—The results of the cryoscopic measurements are given in Table 5.

TABLE 5. *Freezing points of solutions of boric acid and boric oxide in oleum.*

Boric acid.

Solute added (moles)	$H_2S_2O_7$ remaining (moles)	Mole ratio *	F. p.	Solute added (moles)	Mole ratio *	F. p.
	Expt. 115.	Initial wt. of oleum :	127·46 g.			
—	0·02486	—	9·005°	0·01073	0·4318	9·516°
0·00171	0·01973	0·0688	9·166	0·01229	0·4946	9·305
0·00343	0·01456	0·1381	9·335	0·01376	0·5538	9·006
0·00502	0·00978	0·2021	9·457	0·01513	0·6086	8·670
0·00684	0·00434	0·2751	9·604	0·01659	0·6676	8·241
0·00865	—	0·3480	9·671			
	Expt. 116.	Initial wt. of oleum :	126·30 g.			
—	0·02916	—	8·729	0·01066	0·3654	9·505
0·00216	0·02315	0·0739	8·951	0·01314	0·4507	9·276
0·00435	0·01656	0·1492	9·162	0·01508	0·5171	8·965
0·00626	0·01085	0·2145	9·327	0·01668	0·5720	8·590
0·00847	0·00419	0·2906	9·479	0·01813	0·6217	8·233
		Boric oxide.				
	Expt. 122.	Initial wt. of oleum :	145·57 g.			
—	0·02682	—	9·086	0·01022	0·3812	8·843
0·00219	0·02025	0·0817	9·103	0·01374	0·5124	8·310
0·00613	0·00843	0·2286	9·101	0·01839	0·6856	7·542

* Moles of H_3BO_3 (or B_2O_3)/initial moles of $H_2S_2O_7$.

Boric acid. The reactions that would be expected to occur when boric acid is dissolved in an oleum can be deduced from the reaction that occurs in sulphuric acid, which we will assume is reaction (5). Three different successive reactions are to be expected

(I) *Moles of* H_3BO_3*/initial moles of* $H_2S_2O_7 = 0 \rightarrow \frac{1}{3}$.—The initial reaction between boric acid and the disulphuric acid present in the oleum can be represented by the equation

$$H_3BO_3 + 3H_2S_2O_7 = H_3SO_4^+ + B(HSO_4)_4^- + H_2SO_4 \quad . \quad . \quad (9)$$

This equation implies that tetra(hydrogen sulphato)boric acid, $HB(HSO_4)_4$, is sufficiently strong to donate its proton to a sulphuric acid molecule. If this is not so, equation (9) should be replaced by

$$H_3BO_3 + 3H_2S_2O_7 = HB(HSO_4)_4 + 2H_2SO_4 \quad . \quad . \quad . \quad . \quad (10)$$

Equation (9) shows that in this first stage three moles of disulphuric acid are replaced by

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* It should be noted, however, that our measurements do not enable us to distinguish between $B(HSO_4)_4^-$ and any ion containing one boron atom that might be formed from this by addition or removal of sulphuric acid. Dr. P. A. H. Wyatt has recently drawn our attention to one such possibility, namely, $B(HSO_4)_4^- - 2H_2SO_4$, *i.e.*, $B(SO_4)_2^-$. We do not believe that this particular ion is formed in the solutions we have studied because (1) the equilibrium $B(HSO_4)_4^- = B(SO_4)_2^- + 2H_2SO_4$ would be expected to lie over to the left-hand side in the presence of excess of sulphuric acid, (2) analogy with BF_4^- and $B(OH)_4^-$ strongly suggests that $B(HSO_4)_4^-$ should be formed in sulphuric acid, and (3) recently we have attempted to prepare salts of the type $M[B(HSO_4)_4]$ and have concluded that although reactions in which $B(HSO_4)_4^-$ ions lose sulphuric acid do occur in more concentrated solutions than those used in the present work, they are of the type

$$nB(HSO_4)_4^- = [B_n(HSO_4)_{4n-2m}(SO_4)_m]^{n-} + mH_2SO_4$$

and lead to the formation of polymeric anions containing more than one boron atom. The limiting case of such a reaction is when $m = 2n$ and the ion formed is a polymer of the ion suggested above, *i.e.*, $[B(SO_4)_2]_n^{n-}$. Our freezing-point and conductivity measurements are not consistent with the formation of such polymeric ions in the dilute solutions we have investigated. Further work is in progress.

one mole of each of the ions $B(HSO_4)_4^-$ and $H_3SO_4^+$. Now since disulphuric acid is fairly weak,[13]

$$H_2S_2O_7 + H_2SO_4 = H_3SO_4^+ + HS_2O_7^- \quad . \quad . \quad . \quad . \quad . \quad (11)$$

and one stoicheiometric mole of disulphuric acid gives rise to approximately 1·3 total moles of solute particles ($H_2S_2O_7$, $H_3SO_4^+$, and $HS_2O_7^-$), it may be seen that, in this initial reaction, approximately 4 (*i.e.*, 3 × 1·3) moles of solute particles are replaced by 2 moles [$B(HSO_4)_4^-$ and $H_3SO_4^+$]. This reaction should therefore be accompanied by a rise in the freezing point of the solution, and, insofar as our approximation concerning the degree of ionisation of disulphuric acid is correct, the slope of the freezing point–concentration curve would correspond to the loss of two solute particles for each mole of boric acid added and hence to a value of ν for boric acid of $-2{\cdot}00$. At the mole ratio H_3BO_3/initial $H_2S_2O_7 = \frac{1}{3}$, equation (9) shows that the solution contains one mole of $H_3SO_4^+$ and one mole of $B(HSO_4)_4^-$ for each stoicheiometric mole of boric acid. Hence one might expect that the *total* freezing-point depression at this point would correspond to a value of ν for boric acid of 2·00. If equation (10) is correct then at this composition only one mole of solute particles is produced by each mole of boric acid and the total freezing-point depression corresponds to $\nu = 1{\cdot}00$.

(II) *Moles of* H_3BO_3/*initial moles of* $H_2S_2O_7 = \frac{1}{3} \rightarrow \frac{1}{2}$. In this stage the $H_3SO_4^+$ ions produced in stage (I) are replaced by hydroxonium ions and the equation for the reaction may be obtained by imagining that the hydrogen sulphate ions produced by the reaction of boric acid with sulphuric acid (equation 5) react with the $H_3SO_4^+$ ions produced in stage (I) (equation 9). Thus we may write

$$2H_3SO_4^+ + 2B(HSO_4)_4^- + H_3BO_3 + 2H_2SO_4 = 3H_3O^+ + 3B(HSO_4)_4^- \quad . \quad (12)$$

and by combining equations (9) and (12) the overall reaction when the mole ratio is H_3BO_3/initial $H_2S_2O_7 = \frac{1}{2}$ becomes

$$H_3BO_3 + 2H_2S_2O_7 = H_3O^+ + B(HSO_4)_4^- \quad . \quad . \quad . \quad . \quad (13)$$

Equation (12) shows that in this second stage 4 moles of solute particles are replaced by 6 for each mole of boric acid added, and hence the freezing point would be expected to decrease and the slope of the freezing point–concentration curve would be expected to correspond to a value of ν for boric acid of 2·00. At the mole ratio H_3BO_3/initial $H_2S_2O_7 = \frac{1}{2}$, equation (13) shows that there are 2 moles of solute particles [H_3O^+ and $B(HSO_4)_4^-$] for each stoicheiometric mole of boric acid and hence the *total* freezing-point depression at this composition should correspond to a value of ν for boric acid of 2·00.

Since the freezing point rises in stage (I) before the mole ratio H_3BO_3/initial $H_2S_2O_7 = \frac{1}{3}$ is reached and falls in stage (II) after it, there should be a maximum in the freezing point at this composition.

(III) *Moles of* H_3BO_3/*initial moles of* $H_2S_2O_7 > \frac{1}{2}$. Since both the products of the second stage are among the products of the reaction of boric acid with sulphuric acid, no further reaction between the products of stage (II) and additional boric acid can occur, and hence in this third stage the reaction that occurs is the same as that in sulphuric acid, namely (5). As we have seen before, this equation shows that 6 solute particles are produced for each mole of boric acid added, and hence the slope of the freezing point–concentration curve should be greater than in stage (II) and correspond to a value of ν for boric acid of 6·00.

The freezing points of solutions of boric acid in oleum for two different experiments, in which different initial concentrations of oleum were used, are shown in Fig. 2, in which the freezing points of the solution are plotted against the concentration expressed in terms of the mole ratio H_3BO_3/initial $H_2S_2O_7$. It may be seen that in both cases the freezing points rise with increasing concentration of boric acid (*AB*) to a maximum at the mole ratio $\frac{1}{3}$ (*B*). At this point the *total* freezing-point depression, after correction to allow for the depression caused by the products of the self-dissociation of the solvent, corresponds to a value of ν' for boric acid of 2·08 (Table 6). This shows conclusively

TABLE 6. *Values of ν′ for solutions of boric acid and boric oxide in oleum.*

Mole ratio *	m_2	F. p.†, obs.	F. p., corr.	F. p., theor.	ν′	ν, theor.
			Expt. 115. Boric acid.			
$\frac{1}{3}$	0·0669	9·675°	9·737°	9·715°	2·08	2·13
$\frac{1}{2}$	0·1010	9·285	9·438	9·359	1·85	2·00
			Expt. 116. Boric acid.			
$\frac{1}{3}$	0·0796	9·523	9·577	9·552	2·08	2·13
$\frac{1}{2}$	0·1204	9·060	9·213	9·128	1·85	2·00
			Expt. 122. Boric oxide.			
$\frac{1}{3}$	0·6513	8·942	8·980	8·934	4·08	4·20

* Moles of H_3BO_3 (or B_2O_3)/initial moles of $H_2S_2O_7$.
† Values interpolated from graphs of the experimental values.

that the reaction in this first stage cannot be represented by equation (10) which requires ν = 1·00.

Upon further addition of boric acid the freezing point falls (*BC*) and at the mole ratio $\frac{1}{2}$ (*C*) the corrected *total* freezing-point depression corresponds to a value of ν′ for boric acid of 1·85. At higher stoicheiometric concentrations of boric acid the freezing point falls more rapidly (*CD*). All these observations are in accord with the predictions made above.

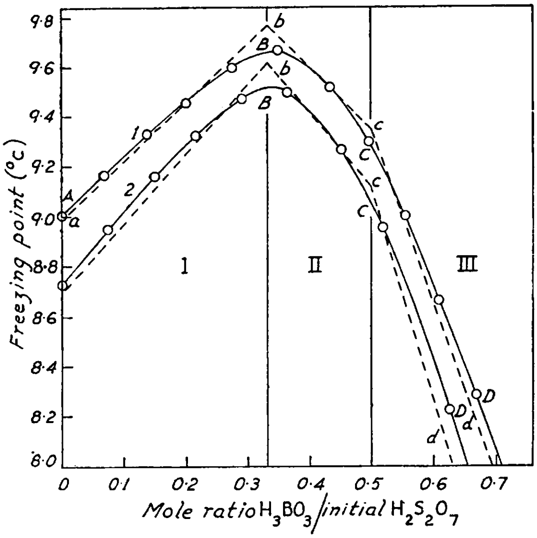

FIG. 2. *Freezing points of solutions of boric acid in oleum.*
1. Expt. 115. 2. Expt. 116.
—○— Observed freezing points *ABCD*.
- - - - Calculated ideal freezing points *abcd*.

For further comparison we have calculated, for the oleum concentrations used in the two experiments, ideal theoretical freezing-point curves based on equations (9), (12), (13), and (5), making the assumptions (i) that the solutions are ideal, (ii) that the solvent does not undergo any form of self-dissociation, and (iii) that in stage (I) the degree of ionisation of disulphuric acid is 33% over the whole composition range involved.[13] These calculated curves are *abcd* in Fig. 2. Thus *ab* has a slope corresponding to a value of ν for boric acid of —2·00 in accordance with equation (9), and the total depression at *b* corresponds to a value of ν of 2·00. In accordance with equation (12), *bc* has a slope corresponding to a value of ν for boric acid of 2·00, and the total depression at *c* corresponds to a value of ν of 2·00 as predicted by equation (13). Finally, *cd* has a slope corresponding to ν = 6·00 in accordance with equation (5). The agreement between the calculated curves *abcd* and the experimental curves *ABCD* is seen to be very good for both experiments.

The differences between the calculated and observed curves may be accounted for as follows. The calculated freezing point *a* is lower than the initial observed freezing point of the oleum *A* mainly because of the approximate nature of our assumption concerning the degree of ionisation of disulphuric acid and the fact that other higher polysulphuric acids, which we have ignored, are present in small concentrations.

At the mole ratio $\frac{1}{3}$ the observed freezing-point maximum B lies below the calculated maximum b. There are two main reasons for this. First, any strong acid HA will actually give rise to slightly more than the expected two particles in solution ($H_3SO_4^+$, A^-) because of the occurrence of the reaction

$$H_3SO_4^+ + H_2SO_4 = H_3O^+ + H_2S_2O_7 \quad . \quad . \quad . \quad . \quad . \quad (14)$$

which is closely related to the ionic self-dehydration reaction and whose equilibrium constant is given by $K = [H_3O^+][H_2S_2O_7]/[H_3SO_4^+]$. Using the value of K_{id} given earlier (p. 1926) and the value of K_a given in Part II,[13] we have

$$K = 2{\cdot}8 \times 10^{-5}/2 \times 10^{-2} = 1{\cdot}4 \times 10^{-3}$$

Thus for our solutions of $H_3SO_4^+,B(HSO_4)_4^-$, whose concentrations are approximately 0·07m, it may be calculated that $\nu = 2{\cdot}13$. Secondly, an additional freezing-point depression is produced by the ions resulting from the partly repressed self-dehydration and autoprotolysis equilibria of the solvent. The observed freezing point B may be corrected for the presence of the ions resulting from the self-dissociation and the corrected value is given in Table 6 and used to calculate the experimental value $\nu' = 2{\cdot}08$. The fact that this value is lower than the predicted theoretical value of 2·13 may be attributed to non-ideal behaviour of the solution.

At the composition corresponding to the mole ratio $\frac{1}{2}$, the observed freezing point C is lower than the calculated value c because of ions resulting from the partly repressed ionic self-dehydration and the unrepressed autoprotolysis. The corrected freezing point (Table 6) is, however, higher than the calculated freezing point C. This implies that in this solution the osmotic coefficient of the solvent is less than unity, which is also indicated by the fact that the experimental ν' is less than the theoretical $\nu = 2{\cdot}00$.

At the highest concentrations investigated the ionic self-dehydration and the autoprotolysis are largely repressed by the solute ions, and the fact that the observed freezing point D is higher than the theoretical freezing point d may be attributed mainly to the non-ideality of the solution.

Boric oxide. The freezing points of solutions of boric oxide in oleum, given in Table 5, are also consistent with the formation of $B(HSO_4)_4^-$. We find that three different successive reactions are to be expected.

(I) *Moles of* B_2O_3/*initial moles of* $H_2S_2O_7 = 0 \rightarrow \frac{1}{3}$. The initial reaction is expressed by the equation

$$B_2O_3 + 4H_2SO_4 + 3H_2S_2O_7 = 2H_3SO_4^+ + 2B(HSO_4)_4^- \quad . \quad . \quad (15)$$

and hence we expect little change in the freezing point of the solution. At the mole ratio B_2O_3/initial $H_2S_2O_7 = \frac{1}{3}$ the *total* freezing-point depression should correspond to a value of ν for boric oxide of 4·00.

(II) *Moles of* B_2O_3/*initial moles of* $H_2S_2O_7 = \frac{1}{3} \rightarrow 1$. In this stage the $H_3SO_4^+$ ions produced in Stage (I) are replaced by hydroxonium ions and the equation for this reaction is

$$H_3SO_4^+ + B(HSO_4)_4^- + B_2O_3 + 7H_2SO_4 = 3H_3O^+ + 3B(HSO_4)_4^- \quad . \quad (16)$$

and by combining equations (15) and (16) it may be seen that the overall reaction at the mole ratio B_2O_3/initial $H_2S_2O_7 = 1$ is

$$B_2O_3 + H_2SO_7 + 6H_2SO_4 = 2H_3O^+ + 2B(HSO_4)_4^- \quad . \quad . \quad . \quad (17)$$

Hence the freezing point would be expected to decrease, and the slope of the freezing point–concentration curve would be expected to correspond to a value of ν for boric oxide of 4·00. At the mole ratio B_2O_3/initial $H_2S_2O_7 = 1$, equation (17) shows that 4 moles of solute particles are produced for each stoicheiometric mole of boric oxide, and hence the *total* freezing-point depression at this composition should correspond to a value of ν for boric oxide of 4·00.

(III) *Moles of* B_2O_3/*initial moles of* $H_2S_2O_7 > 1$. With excess of boric oxide the reaction that occurs is the same as that in sulphuric acid, namely, (6).

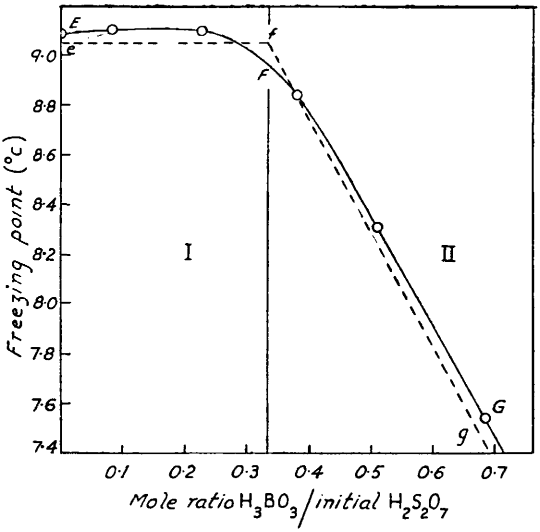

FIG. 3. *Freezing points of solutions of boric oxide in oleum.*

—○— Observed freezing points *EFG*.
– – – – Calculated ideal freezing points *efg*.

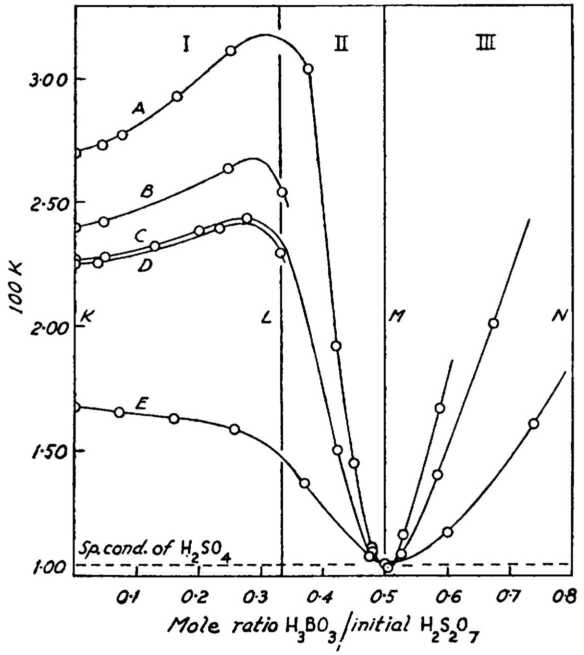

FIG. 4. *Specific conductances of solutions of boric acid in oleum.*

A. Expt. 37.	*D*. Expt. 26.
B. Expt. 27.	*E*. Expt. 8.
C. Expt. 38.	

In Fig. 3 the freezing points of solutions of boric oxide in oleum are plotted against the concentration expressed in terms of the mole ratio B_2O_3/initial $H_2S_2O_7$. It may be seen that the freezing point is almost constant (*EF*) until the composition corresponding to the mole ratio ⅓ is reached (*F*). At this point the *total* freezing-point depression after correction for the additional depression caused by the products of the self-dissociation corresponds to a value of ν for boric oxide of 4·08 as may be seen from Table 6. Upon further addition of boric oxide the freezing point decreases (*FG*). These observations are thus seen to agree with the predictions made above.

For further comparison we have calculated an ideal theoretical freezing-point curve based on equations (14), (15), and (16), and the same assumptions as we made (p. 1931) when considering boric acid solutions. This calculated curve is *efg* in Fig. 3. The agreement between the experimental curve *EFG* and the calculated curve *efg* is good. As before, the differences between the calculated and observed curves may be accounted for in terms of the varying concentrations of the products of self-dissociation of the solvent and deviations from ideal behaviour of the solutions. The experimental ν' value and the theoretical ν value for the mole ratio $\frac{1}{3}$ are given in Table 6.

Conductivity Measurements in Oleum Solutions.—The results of our conductivity measurements in oleum solutions are given in Table 7 and Fig. 4. The three stages in the reaction of boric acid with oleum are clearly shown by the conductivities of the solutions. In stages (I) and (II) the solutions are acid, *i.e.*, they contain more $H_3SO_4^+$ than the pure solvent, while in stage (III) they are basic, *i.e.*, they contain more HSO_4^- than the pure solvent. Thus in stages (I) and (II) the conductivity of the solutions is determined almost completely by the concentration of $H_3SO_4^+$, while in stage (III) it is determined almost completely by the concentration of HSO_4^-.

(I) *Moles of* H_3BO_3/*initial moles of* $H_2S_2O_7 = 0 \rightarrow \frac{1}{3}$. It may be seen from equation (8), bearing in mind that approximately 0·3 mole of $H_3SO_4^+$ ions results from the ionisation of one mole of disulphuric acid, that there will be to a first approximation no change in the number of $H_3SO_4^+$ ions, and hence in the specific conductance, on the addition of boric acid up to the mole ratio $\frac{1}{3}$. It may be seen from Table 7 and Fig. 4 that, in fact, there is either a slight decrease or a slight increase in the conductivity (*KL*), but this is very small compared with subsequent changes and is due mainly to the fact that at low oleum concentrations the degree of ionisation of disulphuric acid is somewhat greater than 33% and at higher oleum concentrations it is somewhat less than this.

TABLE 7. *Specific conductances of solutions of boric acid in oleum.*

Mole ratio *	100κ	Mole ratio *	100κ	Mole ratio *	100κ	Mole ratio *	100κ	Mole ratio *	100κ	Mole ratio *	100κ
Expt. 8. Initial $H_2S_2O_7$: 0·143m.						Expt. 37. Initial $H_2S_2O_7$: 0·537m.					
0·000	1·678	0·257	1·595	0·599	1·177	0·000	2·698	0·250	3·116	0·480	1·116
0·371	1·660	0·371	1·375	0·739	1·616	0·044	2·735	0·334	3·045	0·506	1·031
0·160	1·638	0·475	1·082	0·864	2·040	0·075	2·775	0·419	1·929	0·531	1·164
						0·164	2·934	0·450	1·461	0·587	1·677
Expt. 26. Initial $H_2S_2O_7$: 0·325m.											
0·000	2·254	0·038	2·261	0·233	2·401	0·329	2·302				
Expt. 27. Initial $H_2S_2O_7$: 0·385m.											
0·000	2·403	0·046	2·423	0·246	2·639	0·333	2·544				
Expt. 38. Initial $H_2S_2O_7$: 0·328m.											
0·000	2·266	0·129	2·328	0·277	2·439	0·481	1·089	0·527	1·095	0·673	2·016
0·048	2·280	0·200	2·391	0·424	1·509	0·498	1·050	0·583	1·410		

* Moles of H_3BO_3/Initial moles of $H_2S_2O_7$.

(II) *Moles of* H_3BO_3/*initial moles of* $H_2S_2O_7 = \frac{1}{3} \rightarrow \frac{1}{2}$. Equation (12) shows that in this second stage the highly conducting $H_3SO_4^+$ ion is replaced by the poorly conducting hydroxonium ion and hence the specific conductance of the solution would be expected to decrease with increasing concentration of boric acid. At the mole ratio $\frac{1}{2}$, equation (13) shows that the only ions in the solution are H_3O^+ and $B(HSO_4)_4^-$, apart from those resulting from the self-dissociation of the solvent; hence the specific conductance of the solution would be expected to differ very little from that of sulphuric acid itself. We see from Fig. 4 that the specific conductance in fact decreases rapidly (*LM*) as further boric acid is added after the composition corresponding to the mole ratio $\frac{1}{3}$. At the composition corresponding to the mole ratio $\frac{1}{3}$ the conductivity passes through a minimum value which is approximately the same as that of sulphuric acid itself.

(III) *Moles of* H_3BO_3/*initial moles of* $H_2S_2O_7 > \frac{1}{2}$. In this stage the reaction that occurs is the same as in sulphuric acid itself (equation 5); hydrogen sulphate ions are formed and the conductivity should increase correspondingly. We see in Fig. 4 that in fact the conductivity rises rapidly (*MN*) after the minimum.

If the ionisation of boric acid gives the BO^+ ion then equation (9) for stage (I) should be replaced by

$$H_3BO_3 + 3H_2S_2O_7 = BO^+ + HS_2O_7^- + 4H_2SO_4 \quad . \quad . \quad . \quad (18)$$

and equation (13) for stage (II) should be replaced by

$$H_3BO_3 + 2H_2S_2O_7 = BO^+ + HSO_4^- + 3H_2SO_4 \quad . \quad . \quad . \quad . \quad (19)$$

In this case the ions present at the mole ratio $\frac{1}{3}$ would be BO^+ and $HS_2O_7^-$ and at the mole ratio $\frac{1}{2}$, BO^+ and HSO_4^-. Thus, according to the hypothesis that BO^+ is formed, we should expect the specific conductance to decrease steadily, on the addition of boric acid to an oleum, to a rather small value at the mole ratio $\frac{1}{3}$, and then rise rapidly to a quite large value, because of the presence of the hydrogen sulphate ion, at the mole ratio $\frac{1}{2}$. This is quite contrary to our observations and thus we have further evidence that the ionisation of boric acid does not lead to the formation of BO^+.

The conductivity begins to decrease rather rapidly somewhat before the mole ratio $\frac{1}{3}$ is reached. The explanation of this provides further evidence that the conducting species present at this composition is $H_3SO_4^+$ and not HSO_4^-. This decrease is due to a decrease in the concentration of the $H_3SO_4^+$ ion below its stoicheiometric value as a result of reaction (14) which becomes appreciable as the concentration of $H_2S_2O_7$ is reduced by the added H_3BO_3.

Titrations of Tetra(hydrogen sulphato)boric Acid, $H[B(HSO_4)_4]$, ***with** Potassium Sulphate.*—It may be seen that when sufficient boric acid or boric oxide has been added to an oleum to react with all the disulphuric acid originally present according to equations (9) or (15), one obtains a solution in sulphuric acid of tetra(hydrogen sulphato)boric acid, $H[B(HSO_4)_4]$, which behaves as a strong acid, ionising very substantially, if not completely, according to the equation

$$H[B(HSO_4)_4] + H_2SO_4 = H_3SO_4^+ + B(HSO_4)_4^- \quad . \quad . \quad . \quad . \quad (20)$$

As a strong acid it may be titrated with a base, which is essentially what we have done in adding further boric acid to the solution having a mole ratio H_3BO_3/initial $H_2S_2O_7 = \frac{1}{3}$ as described above and as summarised by equation (12), the end-point of the titration at the mole ratio $\frac{1}{2}$ being indicated by the minimum in the specific conductance and the change in slope of the freezing-point curve. This acid–base reaction is perhaps more strikingly demonstrated by titrating a solution of tetra(hydrogen sulphato)-boric acid with a simple strong base such as $KHSO_4$. For this purpose solutions of $H[B(HSO_4)_4]$ of various concentrations were prepared by adding the calculated quantity of boric acid to oleums whose concentrations were known from their freezing point or conductivity. Successive additions of K_2SO_4 were then made and the conductivity or freezing point measured after each addition.

The results of the conductivity measurements are given in Table 8 and Fig. 5. The specific conductance drops rapidly until $\frac{1}{2}$ mole of K_2SO_4 (*i.e.*, 1 mole of $KHSO_4$) has been added for each mole of $H[B(HSO_4)_4]$ originally present, passes through a minimum at this point, and then rises again. The initial decrease in the specific conductance is due to the removal of the highly conducting $H_3SO_4^+$ ions by the added hydrogen sulphate ions and their replacement by the poorly conducting potassium ion :

$$H[B(HSO_4)_4] + KHSO_4 = K[B(HSO_4)_4] + H_2SO_4 \quad . \quad . \quad . \quad (21)$$

The rise in the conductivity after the minimum is due to the excess of hydrogen sulphate ion. At the point of minimum conductivity, the solution contains the strong electrolyte $K[B(HSO_4)_4]$ and has a specific conductance that differs little from that of sulphuric acid itself : the additional ions are there but they have insignificant mobilities compared to those of the chain-conducting $H_3SO_4^+$ and HSO_4^- ions. It might be thought, therefore, that at the minimum the conductivity would be very slightly greater than that of the solvent whose conductivity is due to the HSO_4^- and $H_3SO_4^+$ resulting from its autoprotolysis. Actually (see Table 8 and Fig. 5) the minimum conductivity is slightly less than that of 100% sulphuric acid. This apparently surprising result must be due to the effect of the relatively high concentration of the potassium ion [and perhaps also the $B(HSO_4)_4^-$ ion] in reducing the mobilities of the HSO_4^- and $H_3SO_4^+$ ions. The reduction of the mobility of the hydrogen sulphate ion by cations has previously been demonstrated[14] and since $H_3SO_4^+$ conducts by the same type of mechanism, it is to be expected that its mobility will be similarly affected.

TABLE 8. *Conductometric titrations of* $HB(HSO_4)_4$ *with* K_2SO_4.

H_3BO_3 * / Initial $H_2S_2O_7$	K_2SO_4 * / Initial $H[B(HSO_4)_4]$	100κ	H_3BO_3 * / Initial $H_2S_2O_7$	K_2SO_4 * / Initial $H[B(HSO_4)_4]$	100κ
Expt. 11.	Initial $H_2S_2O_7$: 0·428m.		Expt. 36.	Initial $H_2S_2O_7$: 0·343m.	
0·000	—	2·492	0·000	—	2·301
0·329	0·000	2·719	0·030	—	2·309
	0·057	2·473	0·091	—	2·340
	0·135	2·141	0·172	—	2·411
	0·225	1·754	0·257	—	2·490
	0·336	1·318	0·331	0·000	2·377
	0·453	1·038		0·132	1·902
	0·492	1·020		0·273	1·419
	0·531	1·047		0·396	1·108
	0·636	1·265		0·480	1·030
	0·708	1·480		0·495	1·031
	0·813	1·818		0·546	1·065
				0·657	1·259
				0·807	1·645

* Mole ratio.

The results of the experiments in which the titrations were followed by means of the measurement of the freezing points of the solutions are given in Table 9 and Fig. 6. It may be seen that the freezing point remains practically constant (*PQ*) on the addition of K_2SO_4 to $H[B(HSO_4)_4]$ until $\frac{1}{2}$ of mole K_2SO_4 (*i.e.*, 1 mole of $KHSO_4$) has been added for each mole of $H[B(HSO_4)_4]$ originally present, after which the freezing point decreases (*QR*).

TABLE 9. *Cryometric titrations of* $H[B(HSO_4)_4]$ *with* K_2SO_4.

Expt. 121. Wt. of oleum, 159·74 g. F. p. of oleum, 8·797°. Initial moles of $H_2S_2O_7$ = 0·03550. Moles of H_3BO_3 added = moles of $H[B(HSO_4)_4]$ formed = 0·01235.

K_2SO_4 added (mmoles)	Moles of K_2SO_4 / Initial moles of $H[B(HSO_4)_4]$	F. p.	K_2SO_4 added (mmoles)	Moles of K_2SO_4 / Initial moles of $H[B(HSO_4)_4]$	F. p.
—	—	9·533°	5·540	0·4681	9·464°
1·246	0·1053	9·542	7·924	0·6696	9·226
3·102	0·2621	9·547			

Mole ratio	H_3BO_3(m)	K_2SO_4(m)	F. p.,* obs.	F. p., corr.	F. p., theor.	ν′	ν, theor.
H_3BO_3/initial $H_2S_2O_7$ = $\frac{1}{3}$	0·07982	—	9·533°	9·587°	9·587°	2·14	2·14
K_2SO_4/initial $H[B(HSO_4)_4]$ = $\frac{1}{2}$ ...	—	0·03783	9·438	9·653	9·663	2·02	2·00

Expt. 141. Wt. of oleum, 164·33 g. F. p. of oleum 8·438°. Initial moles of $H_2S_2O_7$ = 0·04405. Moles of H_3BO_3 added = moles of $H[B(HSO_4)_4]$ formed = 0·01467.

K_2SO_4 added (mmoles)	Moles of K_2SO_4 / Initial moles of $H[B(HSO_4)_4]$	F. p.	K_2SO_4 added (mmoles)	Moles of K_2SO_4 / Initial moles of $H[B(HSO_4)_4]$	F. p.
—	—	9·358°	8·469	0·5773	9·176°
1·987	0·1354	9·374	10·022	0·6969	8·979
4·923	0·3356	9·364	12·590	0·8582	8·671
6·890	0·4697	9·293	14·836	1·0113	8·330
7·339	0·5003	9·268	17·330	1·1813	7·985

Mole ratio	H_3BO_3(m)	K_2SO_4(m)	F. p.,* obs.	F. p., corr.	F. p., theor.	ν′	ν, theor.
H_3BO_3/initial $H_2S_2O_7$ = $\frac{1}{3}$	0·09298	—	9·359°	9·408°	9·389°	2·08	2·12
K_2SO_4/initial $H[B(HSO_4)_4]$ = $\frac{1}{2}$ ...	—	0·04582	9·269	9·484	9·471	1·98	2·00

* Values interpolated from graphs of the experimental values where necessary.

The initial flat portion of the freezing-point curve is in accordance with equation (21) which shows that 2 moles of ions [$H_3SO_4^+$ and $B(HSO_4)_4^-$] are replaced by 2 moles [K^+ and $B(HSO_4)_4^-$] and which predicts, therefore, that no change in the freezing point should occur. The decrease in the freezing point (*QR*) after the addition of ½ mole of K_2SO_4 is due to the ionisation of the excess of potassium sulphate according to the equation

$$K_2SO_4 + H_2SO_4 = 2K^+ + 2HSO_4^- \quad . \; . \; . \; . \; . \quad (22)$$

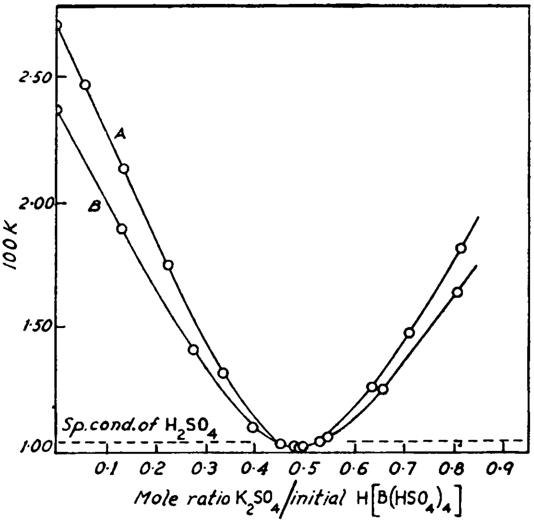

FIG. 5. *Conductometric titrations of* $HB(HSO_4)_4$ with K_2SO_4.
A. Expt. 11. *B*. Expt. 36.

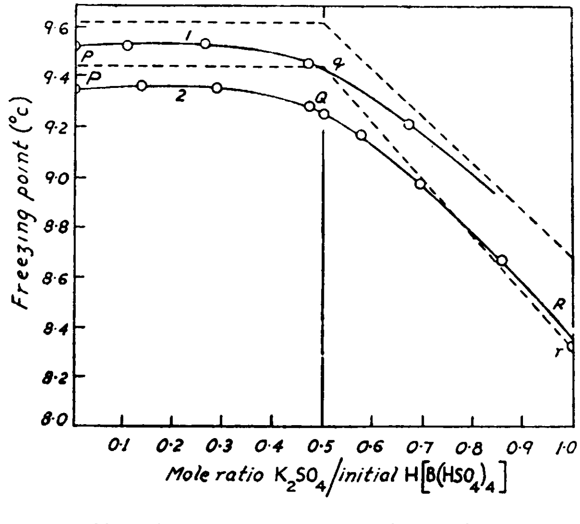

FIG. 6. *Cryometric titrations of* $HB(HSO_4)_4$ [*with* K_2SO_4.
1. Expt. 121. 2. Expt. 141.
—⊙— Observed freezing points *PQR*.
– – – – Calculated ideal freezing points *pqr*.

(Lettering omitted from Curve 1 to avoid confusion.)

The experimental curve *PQR* may be compared with the theoretical curve *pqr* calculated on the basis of equations (21) and (22) and the same assumptions as were made on p. 1931 for the calculation of theoretical curves for boric acid solutions in oleum. Thus *pq* has zero slope in accordance with equation (21) and *qr* has a slope corresponding to $\nu = 4{\cdot}00$ as expected for the ionisation of K_2SO_4 according to equation (22). The agreement between the observed and calculated curves is seen to be good, and the differences may be accounted for satisfactorily in the same manner as we explained in detail for solutions of boric acid in oleum.

It is of interest to note that tetra(hydrogen sulphato)boric acid $H[B(HSO_4)_4]$ is the only known example of a strong acid in the sulphuric acid solvent system. The boron tetra(hydrogen sulphate) ion is the analogue in the sulphuric acid solvent system

$$B(HSO_4)_3 + HSO_4^- = B(HSO_4)_4^-$$

of the borate ion in water

$$B(OH)_3 + OH^- = B(OH)_4^-$$

and of the borofluoride ion in hydrogen fluoride

$$BF_3 + F^- = BF_4^-$$

Raman Spectra.—Solutions of boric acid in sulphuric acid were found to contain a line in their Raman spectra at approximately 1050 cm.$^{-1}$, which increases in intensity with increasing concentration of boric acid, in addition to the known lines of sulphuric acid. This line may confidently be assigned to the hydrogen sulphate ion.[15, 16] Further work on the Raman spectra of these solutions is in progress.

The Raman spectra are thus consistent with the ionisation represented by equation (5).

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[15] Woodward and Horner, *Proc. Roy. Soc.*, 1934, *A*, **144**, 1829.

[16] Ingold, Millen, and Poole, *J.*, 1950, 2576.