915. *Some Cryoscopic Measurements on Solutions of Boron Trifluoride in Sulphuric Acid and Oleum.*

By R. Heckingbottom, B. M. Saunders, I. K. Clark, and J. W. Linnett.

Cryoscopic measurements have been carried out for dilute solutions of boron trifluoride (0·01—0·16 molal) in sulphuric acid containing small amounts (less than 0·09 molal) of either water or disulphuric acid. A static method, based on that developed by Gillespie, was employed. Recorded *i*-factors show considerable variation (4·77—1·54) with composition. A mechanism is suggested to account for the results.

A CONSIDERABLE amount of work has been carried out on solutions of boron trifluoride in sulphuric acid, interest stemming mainly from the fact that both show considerable catalytic activity in many organic reactions. Unfortunately the significance of many of these results is doubtful because the water content of the acid solvent has not been recorded accurately. Recently,[1] the maximum solubility of boron trifluoride in anhydrous sulphuric acid has been determined; it corresponds to $H_2SO_4,0·028BF_3$ and the conductivity of this solution is 0·0055 mho/cm.[3] as compared with 0·0104 mho/cm.[3] for the anhydrous acid.

Only one reaction mechanism has so far been suggested, and this conflicts with the above result. Wichterle, Laita, and Pazlar [2] carried out a rough cryoscopic investigation and recorded a van't Hoff *i*-factor of 2·2, and suggested that $BF_3 + 2H_2SO_4 \rightleftharpoons H_3SO_4^+ + (HSO_4·BF_3)^-$ occurred. The production of $H_3SO_4^+$ ions on this scale would, however, cause an increase in conductivity [3] instead of the observed decrease.

Experimental

Apparatus and Materials.—The design of the cryoscope was based on that developed and described in detail by Gillespie.[4] The lower portion was a sealed off $1\frac{1}{2}$ in. tube with a quick-fit neck. The upper contained a stoppered opening for introducing solute, a sleeve upwards for the stirrer arm and a sleeve downwards and central for the thermocouple junctions. The joint between the two parts was sealed with " Florube W " grease. This was used on all taps, cones, and sockets because of its resistance to boron trifluoride. The internal stirrer consisted of a glass coil which fitted round the thermocouple sleeve; this was attached to a vertical arm containing a small cylinder of iron which was activated by a solenoid controlled by a Thyratron switch.

Temperatures were measured with a multijunction chromel–constantan thermocouple. The wires were insulated with bakelite varnish, and the ends were inserted in glass sheaths subsequently filled with naphthalene which has a high thermal conductivity and also kept the wires in place. The thermocouple was calibrated at the melting point of ice (0·000°c), the transition points of darapskite (13·154°) and of sodium sulphate decahydrate (32·384°). An ice-bath was used for the cold junction. This comprised an outer Dewar vessel containing ordinary ice chips, within which was an inner Dewar containing crushed ice made from distilled water stored in polythene bottles. With this a temperature of $0·000 \pm 0·001°$ could be maintained throughout a run.

The cryoscope was suspended in an air-bath fitted with a side-arm to allow a piece of solid carbon dioxide to be placed against the side of the cryoscope. This air-bath was in turn suspended in a water-bath containing a stirrer and a thermostat. Cooling of the water was effected by adding crushed ice.

The boron trifluoride, supplied in a cylinder, contained up to 0·6% of impurities (0·5% air, 0·08% SO_2, 0·02% SO_3, and 0·003% SiF_4). It was purified by first bubbling it through boric

[1] Greenwood and Thompson, *J.*, 1959, 3643.
[2] Wichterle, Laita, and Pazlar, *Chem. Listy*, 1955, **49**, 1612.
[3] Gillespie and Robinson, *Adv. Inorg. Chem. Radiochem.*, 1959, **1**, 385.
[4] Gillespie, Hughes, and Ingold, *J.*, 1950, 2473.

anhydride in concentrated sulphuric acid. This removed SO_2, SO_3, and any HF or B_2O_3 formed by reaction of boron trifluoride with air contained in the unevacuated line before the bubbler. From the bubbler it passed to a small vertical tube cooled with liquid air. Here the trifluoride solidified and any air could be pumped off. The trifluoride was then allowed to

TABLE 1.

Experimental Results and derived van't Hoff " i " factors.

	Molality H_2O or $H_2S_2O_7$	Molality BF_3	θ (°c)	θ_g (°c)	i factor
Expt. 1	H_2O				
a	0·0480	—	0·312	—	—
b	0·0480	0·051	1·376	1·064	3·4
c	0·0480	0·054	1·442	1·130	3·4
d	0·0480	0·079	1·810	1·498	3·1
e	0·0480	0·106	2·183	1·871	2·9
f	0·0480	0·131	2·493	2·181	2·7
g	0·0480	0·156	2·822	2·510	2·6
Expt. 2					
a	0·0168	—	0·074	—	—
b	0·0168	0·0216	0·704	0·630	4·77
c	0·0291	0·0216	0·743	0·571	4·33
d	0·0413	0·0216	0·778	0·477	3·61
e	0·0637	0·0216	0·889	0·377	2·63
f	0·0872	0·0216	1·113	0·319	2·42
Expt. 3	$H_2S_2O_7$				
a	0·1865	—	1·261	—	—
	H_2O				
b	0·0250	—	0·154	—	—
c	0·0025	—	0·013	—	—
d	0·0025	—	0·018	—	—
e	0·0025	0·0120	0·358	0·340	4·63
f	0·0025	0·0269	0·743	0·724	4·41
g	0·0025	0·0407	1·031	1·013	4·07
h	0·0025	0·0521	1·268	1·250	3·92
i	0·0025	0·0717	1·592	1·547	3·58
Expt. 4	$H_2S_2O_7$				
a	0·1500	—	1·015	—	—
	H_2O				
b	0·0025	—	0·011	—	—
c	0·0025	—	0·018	—	—
d	0·0025	0·0200	0·551	0·533	4·36
e	0·0025	0·0370	0·942	0·924	4·08
f	0·0025	0·0507	1·215	1·197	3·86
g	0·0025	0·0624	1·427	1·409	3·70
h	0·0025	0·0730	1·623	1·605	3·59
Expt. 5	$H_2S_2O_7$				
a	0·0465	—	0·284	—	—
b	0·0440	—	0·266	—	—
c	0·0440	0·0117	0·376	0·110	1·54
d	0·0440	0·0240	0·551	0·285	1·94
e	0·0440	0·0350	0·803	0·537	2·51
f	0·0440	0·0489	1·097	0·831	2·78
g	0·0440	0·0676	1·462	1·196	2·90
Expt. 6					
a	0·0275	—	0·154	—	—
b	0·0280	—	0·160	—	—
c	0·0280	0·0129	0·320	0·160	2·02
d	0·0280	0·0266	0·601	0·441	2·71
e	0·0280	0·0408	0·919	0·759	3·04
f	0·0280	0·0548	1·225	1·065	3·18
g	0·0280	0·0661	1·462	1·302	3·22

evaporate into the storage reservoir. The evaporation was stopped while some trifluoride still remained so that any silicon tetrafluoride would be held back. The reservoir, of measured volume, was immersed in a thermostatted water-bath. Connected to it was a mercury manometer and also a tube leading to the cryoscope. The volume of all the tubing between the reservoir and the cryoscope was carefully measured.

The 98% sulphuric acid used contained less than 0·005% of impurities, other than water. The oleum varied significantly only in sulphur trioxide content. The water used was carefully distilled and stored in polythene bottles.

Procedure.—Oleum was placed in the cryoscope initially and crystallisation was induced by slight supercooling (about 1°) and then touching the side of the cryoscope with solid carbon dioxide. Temperature measurements were made at 30-sec. intervals, or more frequently, from about 5 min. before crystallisation to about ½ hr. afterwards.

Alterations in composition were made by introducing a previously standardised solution of dilute aqueous sulphuric acid from a weight pipette with a long arm which reached down almost to the surface of the liquid. After each addition the cryoscope was closed and left overnight to allow the contents to reach equilibrium before a freezing-point determination was made. When a solvent of required composition had been obtained, the cryoscope was connected to the gas line and the space above the liquid evacuated. Boron trifluoride was then allowed to expand from the reservoir and dead space into the cryoscope. The amount entering was determined from the fall in the pressure in the reservoir and dead space. The cryoscope was then sealed off and left overnight to allow the contents to come to equilibrium so that a freezing-point measurement could be made. Further amounts of boron trifluoride could be introduced as required up to about 0·15 molal.

TABLE 2.

Concentration of species in reactions (vi) and (ix), the degree of dissociation, x, and the v factors.

Run	Molality of species containing B	Molality of H_3O^+ or $H_2S_2O_7$ H_3O^+	Molality of $H_3SO_4^+$	Molality of HSO_3F and SO_3F^-	Degree of dissociation x	v factor
3e	0·0120	0·0304	0·0113	0·0279	0·775	5·65
3f	0·0269	0·0538	0·0113	0·0513	0·635	4·81
3g	0·0407	0·0762	0·0113	0·0677	0·555	4·33
3h	0·0521	0·0835	0·0113	0·0810	0·517	4·10
3i	0·0717	0·0993	0·0113	0·0968	0·450	3·70
		$H_2S_2O_7$				
5c *	0·0117	0·009	0·017	0·35	1	5
		H_3O^+				
5d	0·0240	0·0127	0·0147	0·0568	0·788	4·15
5e	0·0350	0·0291	0·0113	0·0732	0·698	3·93
5f	0·0489	0·0464	0·0113	0·0906	0·617	3·85
5g	0·0676	0·0662	0·0113	0·1104	0·544	3·61
6c	0·0129	0·0067	0·0135	0·0347	0·898	4·59
6d	0·0266	0·0247	0·0113	0·0528	0·663	3·93
6e	0·0408	0·0449	0·0113	0·0721	0·589	3·85
6f	0·0548	0·0616	0·0113	0·0898	0·545	3·76
6g	0·0661	0·0751	0·0113	0·1031	0·520	3·70

* The values for this run are not exact, as the value obtained for x was slightly greater than unity. This is due to the approximations used in the method of allowing for the autodissociation species. Any error due to these approximations is expected to be largest in this instance as a high concentration of autodissociation species is coupled with the lowest measured total change in solute concentration.

Measurement of the freezing point before and after evacuating the space above the acid showed that this did not affect the composition by a detectable amount. It was also apparent that all the boron trifluoride was absorbed because there was no detectable pressure above the acid after leaving overnight; moreover, opening the cryoscope to the vacuum line did not affect the freezing point. Gaseous boron trifluoride diverges from ideality by less than 1% at 20° over the pressure range 0—760 mm., and so the weight of boron trifluoride entering the cryoscope was readily calculated.

Theory of Experiment.—From Gillespie's [5] comparison of results obtained by the static and dynamic methods of cryoscopy, the error in the former can be as high as 5%. Our results are certainly better than this as they include a cooling correction and also an allowance for the heat capacity of the vessel in the supercooling correction. The errors will still be about 1 or 2%,

[5] Gillespie and Bass, *J.*, 1960, 814.

however, and so the simple formula $i = \theta_g/6\cdot12m$, was used. In the formula, i is the van't Hoff factor, $6\cdot12$ is the cryoscopic constant for H_2SO_4, θ_g is the depression due to the added boron trifluoride, and m is its molality.

In the Tables of results i-factors are listed. In the discussion of the mechanism, a v-factor is used. This is the number of particles formed for each molecule of boron trifluoride introduced. Some of these particles may react with or reduce the concentration of the autodissociation species originally present in the acid, so that the net result is that the i-factor is rather less than the v-factor.

The correction of the depression, θ, for cooling was carried out graphically. Allowance was made for the extra solvent separating out with the fall in temperature. Thus the observed cooling was the net effect of the total heat loss and the heat produced by the separation out of more solvent. The supercooling correction can be shown to be:

$$\delta = \frac{\theta S}{\Delta H_f}\left(C_l + \frac{C_v}{M}\right)$$

where θ is the total freezing-point depression measured from $10\cdot371°$, S is the amount of super-cooling, C_l is the heat capacity of sulphuric acid, C_v that of the cryoscope, and M the number of moles of sulphuric acid present. ΔH is the molar heat of fusion of sulphuric acid. For the cryoscope used $\delta = 0\cdot016\,\theta S$.

EXPERIMENTAL RESULTS

Three of the authors operated the apparatus consecutively, each making a preliminary study of the H_2O–SO_3 system in the region of H_2SO_4. This enables a comparison to be made between
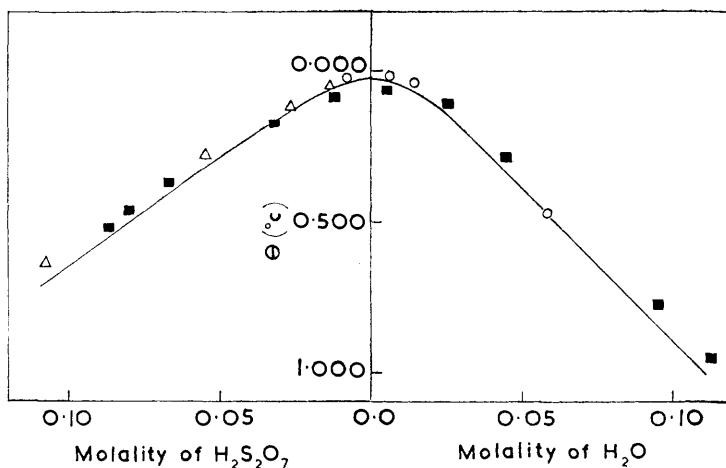
Depression of the freezing point, $\theta°c$, of anhydrous sulphuric acid due to small amounts of either water to disulphuric acid.

Gillespie's curve, ■ Results by B. M. S.; △ Results by I. K. C.; ○ Results by R. H.

our results and those of Gillespie,[6] and served as an internal check on the consistency of our observations. By using these results it was possible to gauge the solvent composition quickly and accurately in subsequent runs. Our results are shown in the Figure where they are compared with Gillespie's curve. Many more results were recorded at higher solute concentrations than shown in the Figure but they cannot be included conveniently on a scale large enough to reveal any differences between our results and Gillespie's. As the solute concentration increases, it is seen that our θ values are less than Gillespie's; this is due to our improved correction terms which bring θ closer to the values observed with the equilibrium method. The only other

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

discrepancy is the low peak obtained by B. M. S.; this was our first run and is probably to be attributed to the presence of small amounts of impurities.

Preliminary results obtained after bubbling boron trifluoride through the solvent until a requisite increase in weight was obtained indicated quite a high i factor, *e.g.*, $i = 4.2$ for a solvent 0.1136 molal in water and 0.0367 molal in boron trifluoride. The method used in this experiment involved changing the cryoscope top for the bubbler top and *vice-versa* and it was thought that water probably entered the cryoscope during these changes. Accordingly the gas line was constructed and further results (expts. 1 to 6) were obtained as described in the experimental section.

Experiment 1 confirmed the high i-factor, and also revealed that it decreased with increasing concentration of boron trifluoride (see Table 1). In runs 1f and 1g, a small back pressure was detected in the cryoscope and, in following experiments, the concentration of boron trifluoride was kept below 0.1 molal.

Experiment 2 showed the striking fall in the i-factor with increasing water content. The run was carried out with dry air in the cryoscope as water could not be added to the evacuated system. In view of the marked effect of any water present, experiments 3 and 4 were carried out with virtually anhydrous acid. Experiment 2 demonstrates that water and boron trifluoride together in sulphuric acid do not produce a depression as great as the sum of their separate effects. Recording all the effect as being due to boron trifluoride is thus somewhat arbitrary, but it gives a ready appreciation of its magnitude.
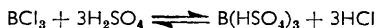
Experiment 3 shows the effect of boron trifluoride in anhydrous sulphuric acid and 4 confirms these results. Between runs 3c and 3d, and between 4b and 4c the cryoscope was evacuated producing the small change in 0 shown.

Experiments 5 and 6 were conducted in oleum. In experiment 5 evacuation carried out between runs 5a and 5b did cause a slight loss in sulphur trioxide and so experiment 6 was carried out at a lower $H_2S_2O_7$ concentration. After 5c and subsequent runs there was no detectable back pressure in the cryoscope showing that there were no further losses due to evacuation.
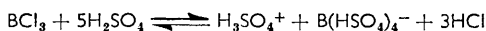
DISCUSSION

The low solubility of boron trifluoride in sulphuric acid suggests that only a portion of the trifluoride introduced will react with the solvent; the experiments described here were carried out at concentrations which were in the range $\frac{1}{20}$ to $\frac{1}{2}$ of that for the saturated solution; only those below $\frac{1}{4}$ of that strength are discussed quantitatively (see above). This means that, though the i-factor is itself high, the number of particles produced from each boron trifluoride molecule that *does* react with the solvent is most probably even larger than this.

Two kinds of dissociation equilibria have been suggested for solutes similar to boron trifluoride in sulphuric acid. These may be exemplified by using boron trichloride and NO_2F. In the first case it seems well established [1] that boron trichloride reacts according to
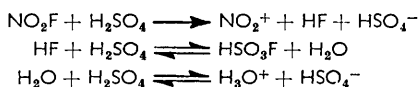
$$BCl_3 + 3H_2SO_4 \rightleftharpoons B(HSO_4)_3 + 3HCl$$

or

$$BCl_3 + 5H_2SO_4 \rightleftharpoons H_3SO_4^+ + B(HSO_4)_4^- + 3HCl$$

depending on the proportions of the reactants. Gillespie [7] has also shown that $B(OH)_3$ and B_2O_3 form $B(HSO_4)_4^-$ in sulphuric acid. Analogy between boron trifluoride and these compounds can only be limited however, despite the inter-changeability of F and OH when boron trifluoride is in aqueous solutions. Boron trifluoride reacts much less vigorously, and to a more limited extent than other solutes. Also, it decreases the conductivity whereas the other solutes increase it considerably.

The second possible type of solute behaviour is that suggested for NO_2F. In concentrations lower than 0.1 molal the mechanism that has been suggested [8] is:

$$NO_2F + H_2SO_4 \longrightarrow NO_2^+ + HF + HSO_4^-$$
$$HF + H_2SO_4 \rightleftharpoons HSO_3F + H_2O$$
$$H_2O + H_2SO_4 \rightleftharpoons H_3O^+ + HSO_4^-$$

[7] Gillespie, Flowers, and Oubridge, *J.*, 1956, 1925.
[8] Hetherington, Hub, and Robinson, *J.*, 1955, 4041.

It was claimed that this explained the observed i-factor of 5, and also the increase in conductivity. However more recent work by Gillespie [3] casts doubt on this explanation as he has shown that HSO_3F dissociates according to
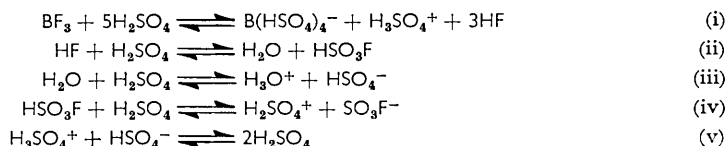
$$HSO_3F + H_2SO_4 \rightleftharpoons H_3SO_4^+ + SO_3F^-$$

the dissociation constant K being 3×10^{-3} mole/l. The net result of including this is to reduce the i-factor to 4 because, in effect HSO_3F removes HSO_4^- by

$$HSO_3F + HSO_4^- \rightleftharpoons SO_3F^- + H_2SO_4$$

The effect of this change would also mean that the mechanism failed to explain the conductivity increase observed. Nevertheless there is good evidence for the formation of NO_2^+ and hence for the removal of F^- by the acid solvent. However, in the present context, it must be remembered that NO_2F is much more soluble than BF_3 and that they have opposite effects on the conductivity.

From the present results it is proposed that the following processes occur:

$$BF_3 + 5H_2SO_4 \rightleftharpoons B(HSO_4)_4^- + H_3SO_4^+ + 3HF \qquad \text{(i)}$$
$$HF + H_2SO_4 \rightleftharpoons H_2O + HSO_3F \qquad \text{(ii)}$$
$$H_2O + H_2SO_4 \rightleftharpoons H_3O^+ + HSO_4^- \qquad \text{(iii)}$$
$$HSO_3F + H_2SO_4 \rightleftharpoons H_2SO_4^+ + SO_3F^- \qquad \text{(iv)}$$
$$H_3SO_4^+ + HSO_4^- \rightleftharpoons 2H_2SO_4 \qquad \text{(v)}$$

If (i), (ii), (iii), and (v) go completely to the right and (iv) takes place to an extent sufficient to remove all the HSO_4^- by reaction (v) the resultant equation is:

$$BF_3 + 7H_2SO_4 \longrightarrow B(HSO_4)_4^- + 3H_3O^+ + HSO_3F + 2SO_3F^- \qquad \text{(vi)}$$
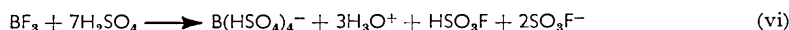
each BF_3 molecule leading to the production of 7 solute ions. At this stage, because a considerable amount of SO_3F^- is present, reaction (iv) will in fact overshoot this position by only a very small amount.

In the solutions actually being studied, (iii) and (v) will be expected to go virtually to completion, and (ii) nearly so at the concentration used,[9] though it will be sensitive to changes in these concentrations. The reaction of boron trifluoride with the solvent will not go to completion however. This is made clear by the fact that boron trifluoride can be prepared commercially by the process:

$$B(OH)_3 + 3HSO_3F \rightleftharpoons BF_3 + H_2SO_4$$
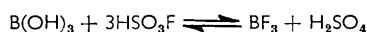
with or without the presence of sulphuric acid. We may therefore expect the reaction:

$$3H_3O^+ + 3HSO_3F + B(HSO_4)_4^- \rightleftharpoons BF_3 + 5H_2SO_4 + 2H_3SO_4^+ \qquad \text{(vii)}$$
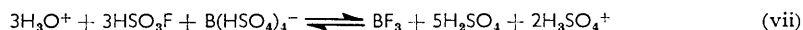
to occur to some extent with a consequent reduction in the number of solute species (in addition, intermediate species such as $BF(HSO_4)_3^-$, $BF_2(HSO_4)_2^-$, etc., may be produced). In effect, with (ii), reaction (vii) is a reversal of (i). It will be shown that the maximum i-factors observed in the absence of water can be explained if about four-fifths of the boron trifluoride dissociates.

Whenever a solute reacts with a solvent to give a *greater* number of species and there is an equilibrium between the solute and solvent on the one hand and the products on the other, the extent of reaction will decrease with increasing concentration of the solute. Therefore the fact that the observed i-factors decreases with increasing concentration of boron trifluoride confirms that reaction with the solvent is incomplete. Also since, with decreasing concentration there is no sign of the experimental i-factor approaching a limiting

[9] Lange, " Fluorine Chemistry," Vol. I, Academic Press Inc., N.Y., 1950, p. 169.

value, the number of species produced from each boron trifluoride molecule actually reacting completely must be greater than the highest observed i-factor (4·8), and presumably considerably greater. The suggested figure of 7 is therefore consistent with the observed change in i with the concentration of boron trifluoride.

The fall in i-factor with increasing water concentration is also to be expected. This may be thought of as being due to a shift to left of reaction (ii) with its consequent effect on (i). Alternatively, since H_2O will form H_3O^+ with the solvent [reaction (iii)], it may be considered in terms of the overall equation which shows that the presence of H_3O^+ will have a considerable effect in reducing the reaction of boron trifluoride with the solvent.

The very different i-factors observed in oleum are also explained by this mechanism. The hydrogen fluoride formed by reaction (i) will react either directly with disulphuric acid
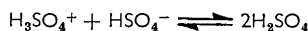
$$HF + H_2S_2O_7 \rightleftharpoons HSO_3F + H_2SO_4$$
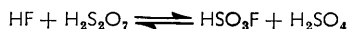
or with the solvent by (ii) and (iii). Disulphuric acid reacts with solvent according to

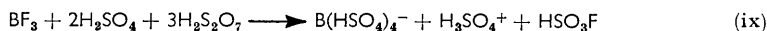$$H_2S_2O_7 + H_2SO_4 \rightleftharpoons HS_2O_7^- + H_3SO_4^+ \qquad \text{(viii)}$$
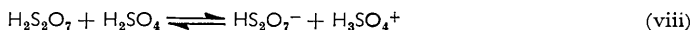
for which $K = 1·4 \times 10^{-2}$. The products of reaction (iii) will react with the products of the above reaction by

$$HS_2O_7^- + H_3O^+ \rightleftharpoons 2H_2SO_4$$

and

$$H_3SO_4^+ + HSO_4^- \rightleftharpoons 2H_2SO_4$$
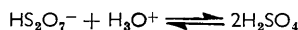
If the boron trifluoride reacts completely, the resultant effect of the processes occurring, when oleum is present, is

$$BF_3 + 2H_2SO_4 + 3H_2S_2O_7 \longrightarrow B(HSO_4)_4^- + H_3SO_4^+ + HSO_3F \qquad \text{(ix)}$$

Thus each boron trifluoride, in these circumstances, produces five solute species. As the above equation is written, with $H_2S_2O_7$ on the left-hand side, the i-factor is 2. However, the $H_2S_2O_7$ will in fact, have reacted with the solvent according to equation (viii) above. Nevertheless it is incorrect to think of each $H_2S_2O_7$ simply producing two new species ($H_3SO_4^+$ and $HS_2O_7^-$) because the production of these reduces the autodissociation of the solvent. The situation is complex but it is clear that overall each $H_2S_2O_7$ adds fewer than two new species. The exact number depends on the concentration, but is always much less than two.

Experiments 5 and 6 show that, when boron trifluoride is added to oleum, the i-factor is small but rises with increase in the amount of boron trifluoride added. In the last paragraph it was shown that the low value obtained when small amounts are added is understandable. The increase as more is added is due to the fact that, as $H_2S_2O_7$ is removed by BF_3, the BF_3 reacts increasingly directly with solvent [*i.e.*, by reaction (vi)].

It is possible to make allowance for the effects on the autodissociation of the solvent in a more quantitative manner by using Tables prepared by Gillespie.[10] By doing this it is possible to calculate the extent to which the solute has reacted with the solvent and "dissociated." In anhydrous acid, if x is the fraction of BF_3 reacted, and reactions (ii), (iii), and (v) go to completion while (iv) occurs until no free HSO_4^- remains, then $v = 1 + 6x$. As a first approximation, a value for x was obtained by using $i = 1 + 6x$ (*i.e.*, any effects on the autodissociation of the solvent are ignored). This value of x is used to calculate the amount of water formed. By using this together with Gillespie's Tables [10] it is possible to estimate the concentrations of all the species produced by solvent dissociation (H_3O^+, HSO_4^-, $H_3SO_4^+$, and $HS_2O_7^-$). If the total concentration of these species is m_d, the v factor may be calculated by using

$$v = \frac{\theta_r}{6·12m} - \frac{m_d}{m}$$

[10] Gillespie, Bass, and Robinson, *J.*, 1960, 821.

where θ_r is the total depression measured from $10 \cdot 625°$ (the freezing point calculated by Gillespie for undissociated H_2SO_4) and m is the molality of the BF_3 introduced. This value of v can be used to calculate a new value of x and the calculation repeated. This cycle is repeated until consistent values of v and x are obtained. These final v and x values are listed in the first section of Table 2 and provide a much better estimate of the true v and x because allowance has been made for the effects on the dissociation of the solvent. It can be seen that in the most dilute solution $v = 5 \cdot 65$. The fact that this is greater than 5 rules out some other possibilities that might have been considered (cf. NO_2F).

An analogous treatment can be carried out for solutions in oleum. When $H_2S_2O_7$ remains after adding BF_3, the first approximation is $i = 1 + x$. By using this value of x, the amount of $H_2S_2O_7$ left and $H_3SO_4^+$ formed were calculated and then the effect on solvent autodissociation allowed for, and a value for $v = (1 + 4x)$ obtained. Successive approximation was used as before to obtain self-consistent values.

For solutions in which the amount of boron trifluoride added was just sufficient to react with the $H_2S_2O_7$ present, some excess of $H_3SO_4^+$ will remain (*i.e.*, the amount of HSO_4^-, formed by reaction of HF with H_2SO_4, remaining after reaction with the oleum will not be as great as the amount of $H_3SO_4^+$ formed by (ix). At this stage $i = 1 + 4x - y$, where ym is the amount of oleum removed; y does not appear in the expression for v. With the addition of more BF_3, the $H_3SO_4^+$ formed in (ix) is removed and the same reaction as that in anhydrous acid takes place except for the species removed by reaction with $H_2S_2O_7$. Under these circumstances $i = 1 + 6x - 2y$ and $v = 1 + 6x - y$. The results of the calculations for the oleum solutions (experiments 5 and 6) are also shown in Table 2. The results for experiment 4 are similar to those for 3 and consequently are not included. Those for experiment 3 show that x and v fall as H_3O^+ and HSO_3F build up, and also that there is considerable suppression of the production of species by autodissociation (*e.g.*, for experiment reaction 3e $v = 5 \cdot 65$ whereas $i = 4 \cdot 63$). A comparison of experiment 5d with 3e shows the effect of $H_3SO_4^+$ and HSO_3F in reducing x; whereas the values of x are comparable, the water concentration in experiment 5d is much lower, but the concentration of $H_3SO_4^+$ and HSO_3F, which will also cause a reduction of x, are higher. A comparison of the results for experiment 6 with those for 3 (6c with 3c) confirms that, for approximately the same content of boron trifluoride, x is higher when some of the water formed has been removed by oleum, but that when water concentrations are comparable (experiments 6d and 3e) x is lower in the oleum solutions due to the higher concentrations of BF_3 and HSO_3F there.

The suggested mechanism accounts satisfactorily for the cryoscopic measurements. It is also compatible with the fall in the conductivity of solutions in anhydrous acid as, despite the high i factor, there is virtually no increase in the concentrations of $H_3SO_4^+$ and HSO_4^{--}, the species mainly responsible for conducting electricity in sulphuric acid, a " proton jump " process taking place analogous to that occurring in water. Moreover, several species are produced, when BF_3 is added [HSO_3F, SO_3F^- and $B(HSO_4)_4^-$], which might interfere with the proton jump process and so reduce the conductivity.

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