

605. *Bromine Trifluoride as an Ionizing Solvent.*

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The existence of the ionic equilibrium $2\text{BrF}_3 \rightleftharpoons \text{BrF}_2^+ + \text{BrF}_4^-$ in liquid bromine trifluoride is supported by the isolation of "acids" and "bases" containing the BrF_2^+ and BrF_4^- ions, respectively. The compounds BrF_2SbF_6 and $(\text{BrF}_2)_2\text{SnF}_6$ behave as acids, and the bromofluorides KBrF_4 , AgBrF_4 , and $\text{Ba}(\text{BrF}_4)_2$ as bases. Conductivity measurements on bromine trifluoride solutions of these compounds are described, and it is shown by conductometric titrations that neutralisation reactions can occur to produce salts containing the SbF_6^- and SnF_6^{--} anions.

THE electrical conductivity of pure bromine trifluoride has been attributed to the ionic equilibrium $2\text{BrF}_3 \rightleftharpoons \text{BrF}_2^+ + \text{BrF}_4^-$ (Banks, Emeléus, and Woolf, preceding paper) which is analogous to that existing in water, ammonia, and other solvents, such as nitrogen dioxide, for which the equilibrium $2\text{NO}_2 \rightleftharpoons \text{NO}^+ + \text{NO}_3^-$ has recently been postulated (Addison and Thompson, *Nature*, 1948, **162**, 369). By extension of the terminology introduced by Franklin for the ammonia system (*J. Amer. Chem. Soc.*, 1905, **27**, 820), substances which contain the ions BrF_2^+ and BrF_4^- are regarded as acids and bases, respectively.

Three well-defined bases have already been described, for there is clear evidence that the compounds KBrF_4 , AgBrF_4 , and BaBr_2F_8 (Sharpe and Emeléus, *J.*, 1948, 2135) contain the BrF_4^- ion. This is based on (i) the association of two BrF_4 units with the invariably bivalent element barium, (ii) the absence of potassium bromide and potassium fluoride lines from X-ray powder photographs of the potassium compound, (iii) the stability to heat and to organic liquids, and (iv) the analogy with KICl_4 , known to contain the ICl_4^- ion (Mooney, *Z. Krist.*, 1938, **98**, 377), which undergoes a thermal decomposition into potassium chloride and iodine trichloride similar to that of potassium bromotetrafluoride (tetrafluorobromate) into potassium fluoride and bromine trifluoride.

The conductivity of bromine trifluoride is also increased by the addition of bromofluorides in much the same way as that of iodine monochloride is increased by dissolved chlorides (Cornog and Karges, *J. Amer. Chem. Soc.*, 1932, **54**, 1882). The bromofluoride solutions differ from the pure solvent in possessing a positive temperature coefficient of conductivity and in disobeying Ohm's law. They also have a linear temperature variation of equivalent conductivity. Such measurements, although not allowing a distinction to be made between the existence of a BrF_4^- or a F^- ion in solution, provide useful criteria with which the properties of acid solutions can be compared.

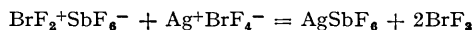
A compound SbBrF_6 has been prepared by the reaction of bromine trifluoride with antimonous oxide or fluoride or with antimonyl chloride. The evidence that it is an acid $\text{BrF}_2^+\text{SbF}_6^-$ rather than an addition compound $\text{SbF}_5\cdot\text{BrF}_3$ is similar to that presented for bases. Thus the conductivity of bromine trifluoride increases on adding the antimony compound, showing that ions are produced. In this case further conclusions can be drawn about the nature of the ions

since it is unlikely that the ions are formed from antimony pentafluoride ($\text{SbF}_5 \rightleftharpoons \text{SbF}_4^+ + \text{F}^-$) present in an addition compound. The pentafluoride itself has a specific conductivity of less than 10^{-9} ohm $^{-1}$ cm. $^{-1}$ (N. Greenwood, unpublished observations). These acid solutions resemble those of bases in having positive temperature coefficients, linear variation of equivalent conductivity with temperature, and ill-defined decomposition potentials.

The stable character of the bound bromine trifluoride in the antimony compounds is shown by the fact that it melted and began to decompose at about 200°, a temperature above the boiling points of either bromine trifluoride (127°) or antimony pentafluoride (150°) both of which, unlike the antimony compound, react violently with organic liquids.

The SbF_6^- ion is well known in the alkali salts (Marignac, *Annalen*, 1868, **145**, 237), and a compound $\text{SbF}_5 \cdot \text{NOF}$ prepared by Ruff, Stauber, and Graff (*Z. anorg. Chem.*, 1908, **53**, 325) probably has the structure $(\text{NO})^+\text{SbF}_6^-$, analogous to the new compound $(\text{BrF}_2)^+\text{SbF}_6^-$, in view of the existence of positive nitrosyl ions in what were once thought to be addition compounds. Thus in the case of the compounds $\text{SnCl}_4 \cdot 2\text{NOCl}$ and $\text{SbCl}_5 \cdot \text{NOCl}$, the first is isomorphous with ammonium stannichloride (Klinkenberg, *Rec. Trav. chim.*, 1937, **56**, 749) while the second is able to increase the conductivity of liquid nitrosyl chloride (Burg and Campbell, *J. Amer. Chem. Soc.*, 1948, **70**, 1964). An ionic formulation as $(\text{NO})_2\text{SnCl}_6$ and $(\text{NO})\text{SbCl}_6$ seems therefore to be justified.

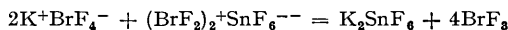
Reaction in bromine trifluoride solution between a base, silver bromofluoride (tetrafluorobromate), and the antimony acid has been found to yield the salt AgSbF_6 according to the equation



Barium and potassium bromofluorides gave the corresponding fluoroantimonates, which were, however, contaminated with solvent.

A conductometric titration of silver bromofluoride with the antimony acid in bromine trifluoride solution gave a sharp end-point when equimolecular amounts of acid and base were present. The shape of the titration curve and the position of the end-point are explicable in terms of a neutralisation process. The initial value of the conductivity is due to the ions Ag^+ and BrF_4^- , together with those of the solvent, and the fall in conductivity as neutralisation is approached is due to replacement of BrF_4^- by the larger, less mobile, SbF_6^- ion. The radii of these ions, calculated from the covalent radii of the elements, are: SbF_6^- , 2.64 Å.; BrF_4^- , 2.39 Å. On passing the equivalence point the conductivity rises because of the addition of BrF_2^+ and SbF_6^- ions. The slope of the branch of the titration curve is in fact the same as that for solutions of SbBrF_8 in bromine trifluoride.

It has not yet proved possible to isolate other acids in a pure state. The reaction between bromine trifluoride and stannous or stannic chloride, or tin, gave solutions from which, on pumping off the excess bromine trifluoride at room temperature, a product of the composition $\text{SnF}_4 \cdot 1.76\text{BrF}_3$ was obtained. At 190° all of the bromine trifluoride was removed. The bound bromine trifluoride in the tin compound showed its resemblance to that in the bases and in the antimony acid by its mild reaction with water and organic liquids. The difference between the antimony and the tin compound was similar to that between the bromofluorides of potassium and calcium, since bromine trifluoride is readily pumped off from the latter so that a stoichiometric compound cannot be isolated. Salt formation occurred on allowing bases to react with stannous chloride solutions in bromine trifluoride. It was also found that on titrating potassium bromofluoride with stannous chloride in bromine trifluoride the conductivity was a minimum when the molecular ratio of the potassium and the tin compound was 2 : 1. These results correspond with a neutralisation reaction involving the acid $(\text{BrF}_2)_2\text{SnF}_6$



EXPERIMENTAL.

Conductivity measurements were made in the same way as those for bromine trifluoride (Banks, Emeléus, and Woolf, *loc. cit.*). At first, solutions were prepared directly in the cell by distilling bromine trifluoride in vacuum on to a weighed quantity of solid, the weight of solvent being given by the loss in weight of the silica trap from which it had been distilled. This procedure, although ensuring the absence of traces of water, was both time consuming and inaccurate on account of weighing errors. For the majority of the experiments, solutions were made from a weighed amount of solid in a small silica flask, using freshly distilled bromine trifluoride and heating for about one minute to ensure complete solution and remove volatile reaction products such as chlorine from chlorides. The flask was then attached to the vacuum line, and 1—2 c.c. of solvent were distilled over in vacuum to eliminate traces of volatile impurities.

Conductivity data for the potassium, silver, and barium salts are given in Tables I and II. In Table I

the conductivity of the solvent is subtracted from that of the solution, the values obtained previously (Banks, Emel us, and Woolf, *loc. cit.*) being used. The temperature variation for these figures is linear. The variation of equivalent conductivity as a function of concentration is not included since, although they show certain interesting features, their significance is not clear at this stage of the investigation.

TABLE I.
Specific conductivity of KBrF₄ in BrF₃ solution.

Concn., g.-mol./1000 g. BrF ₃ .		Conductivity of Solution — Solvent.		Concn., g.-mol./1000 g. BrF ₃ .		Conductivity of Solution — Solvent.	
Temp.	Solution.	Solvent.	Temp.	Solution.	Solvent.	Solution.	Solvent.
Solutions made with KF.				Solutions made with KCl.			
0-0159	15-0°	9-88	1-86	0-0108	10-0°	8-96	0-83
	25-0	10-34	2-34		16-9	9-12	1-02
	35-0	10-55	2-78		25-0	9-28	1-28
	45-0	10-69	3-26		34-9	9-29	1-51
	55-0	10-83	3-80		49-0	9-28	2-01
0-0309	10-0	12-30	4-17	0-0182	10-8	10-08	1-97
	13-9	12-65	4-53		16-7	10-34	2-24
	14-6	12-70	4-58		25-0	10-63	2-63
	20-0	13-10	5-02		34-3	10-84	3-05
	25-0	13-45	5-45		44-2	11-01	3-55
	35-0	14-20	6-43				
	45-0	14-60	7-17	0-0435	10-2	14-86	6-73
					17-9	15-79	7-69
0-0580	15-0	18-30	10-18		25-0	16-61	8-61
	21-8	19-30	11-24		35-9	17-71	9-96
	25-0	19-80	11-80		47-2	18-67	11-33
	35-0	21-10	13-33				
	45-0	22-40	14-97	0-0778	9-3	20-63	12-50
					17-2	22-37	14-37
					25-0	24-03	16-03
					35-4	25-99	18-43
					44-3	27-60	20-15

TABLE II.

Concn., g.-mol./1000 g. BrF ₃ .	Temp.	Sp. cond., ohm ⁻¹ cm. ⁻¹ × 10 ³ .	Concn., g.-mol./1000 g. BrF ₃ .	Temp.	Sp. cond., ohm ⁻¹ cm. ⁻¹ × 10 ³ .
(a) <i>Conductivity of AgBrF₄ in BrF₃ solution.</i>					
0-0140	10-2°	9-62	0-0582	10-4°	16-79
	16-5	9-79		14-7	17-40
	25-0	9-97		25-0	18-65
	35-1	10-04		35-6	19-77
	44-5	10-01			
0-0367	9-9	12-58	0-0812	10-7	21-55
	17-0	13-16		17-2	22-40
	25-0	13-70		25-0	23-87
	34-0	14-20		32-7	25-10
	45-7	14-64		33-5	25-20
				41-7	26-40
(b) <i>Conductivity of Ba(BrF₄)₂ in BrF₃ solution.*</i>					
0-00298	25-0	8-26	0-0294	10-0°	12-94
	35-4	8-03		17-7	13-43
	43-8	7-78		25-0	14-01
				35-0	14-12
0-01510	10-0	10-03		45-6	14-21
	17-7	10-23			
	25-0	10-46	0-0676	9-5	20-06
	34-0	10-31		17-7	21-57
	47-0	9-97		25-0	22-86
				34-5	23-85
				45-9	24-89

* The measurements with the potassium and silver salts were reproducible on varying the temperature, but in the case of the barium salt the value at 25° was only reproducible within 5% after the solution had been heated to the maximum temperature.

Several series of measurements were made of the current passing in a solution of potassium fluoride in bromine trifluoride at various direct current voltages in order to establish whether Ohm's law was

obeyed. The following typical data show that this was not the case (concn.: 0.0309 g.-mol. of $\text{KBrF}_4/1000 \text{ g.}$):

Voltage	0.10	0.20	0.40	0.60	0.80	1.00	2.00	3.00	4.00
Current (milliamp.)	0.05	0.14	0.31	0.52	0.77	1.05	2.34	3.82	5.34
$10^{-3} V/C$	2.00	1.43	1.29	1.15	1.04	0.95	0.85	0.79	0.75

In these experiments, after a period of electrolysis, a brown colour developed at the cathode which was separated from the unchanged yellow liquid in the remainder of the cell by a sharp boundary.

The Preparation of the "Acid" Compounds SbBrF_8 and $\text{SnBr}_2\text{F}_{10}$.—Antimony trifluoride, made from antimonous oxide and hydrofluoric acid, or antimonous oxide, was allowed to react with bromine trifluoride in a silica flask. In the first case reaction was mild, bromine being set free as would be expected in the oxidation of antimony to the quinquivalent state. The oxide reacted violently and oxygen was evolved. The reaction was moderated by adding bromine as a diluent. In each case excess of bromine trifluoride and free bromine was pumped off in vacuum at room temperature until constant weight was attained. The yellow product was analysed for bromine by decomposition with water in a stoppered bottle, followed by reduction with sulphurous acid and precipitation of silver bromide. Fluorine was determined by decomposing the solid with sodium carbonate solution, keeping the mixture overnight to ensure complete reaction, and precipitating the fluoride formed as calcium fluoride. Antimony was precipitated as sulphide, which was dissolved in concentrated hydrochloric acid and titrated with a standard potassium bromate solution. The equivalent weight was calculated from the ratio of the weight of the antimony compound taken to that of the product (Found, for product from Sb_2O_3 : Sb, 34.6; Br, 22.8; F, 42.5%; equiv., 350. Found, for product from SbF_3 : Br, 22.8; F, 42.3%; equiv., 349. SbBrF_8 requires Sb, 34.4; Br, 22.6; F, 43.0%; equiv., 354). The stability of *antimony bromo-octafluoride (octafluorobromate)* was shown by heating a 2.2429-g. sample for 2 hours in a vacuum at 40° , whereupon the loss in weight was 0.0021 g.

Antimonyl chloride gave a product which was qualitatively the same, though in this case the reaction with bromine trifluoride was even more violent than that of the oxide. The compound was decomposed by water, giving a solution with oxidising properties which probably contained the hexafluoroantimonate ion since characteristic antimony reactions were masked. For instance, a precipitate appeared after boiling with ammonia only on long storage, and there was an appreciable time lag in the reaction with hydrogen sulphide. The solid fumed in moist air, its colour changing to a deep red. It could be stored in dry Pyrex glass for several months without appreciable attack on the vessel.

TABLE III.

Concn., g.-mol./ 1000 g. BrF_3 .	Temp.	Sp. cond., $\text{ohm}^{-1}\text{cm.}^{-1}$ $\times 10^3$.	Concn., g.-mol./ 1000 g. BrF_3 .	Temp.	Sp. cond., $\text{ohm}^{-1}\text{cm.}^{-1}$ $\times 10^3$.	Concn., g.-mol./ 1000 g. BrF_3 .	Temp.	Sp. cond., $\text{ohm}^{-1}\text{cm.}^{-1}$ $\times 10^3$.
(a) <i>Conductivity of SbBrF_8 in BrF_3.</i>								
0.00535	9.7°	11.36	0.0178	10.8°	15.76	0.0306	10.0°	18.96
	16.4	11.59		16.9	16.28		17.1	19.81
	25.0	11.79		25.0	16.88		25.0	20.67
	34.3	11.88		35.5	17.42		34.1	21.37
	45.9	11.86		45.5	17.76		47.0	22.33
0.00614	10.2	11.06	0.0220	10.0	16.46	0.0448	9.5	23.92
	17.1	11.25		17.7	17.16		17.2	25.28
	25.0	11.42		25.1	17.75		25.0	26.52
	36.8	11.48		36.0	18.41		36.2	27.99
	52.5	11.35		46.0	18.85		47.0	29.15
(b) <i>Conductivity of $\text{SnBr}_2\text{F}_{10}$ in BrF_3.</i>								
0.00910	10.2°	10.81	0.0234	9.3°	15.16	0.0494	10.6°	22.38
	16.7	10.91		17.2	15.59		16.9	23.12
	25.0	10.95		25.0	15.86		25.0	23.90
	35.4	10.81		35.8	16.01		35.4	24.60
	48.8	10.46		44.9	15.91		44.9	24.94
0.0152	9.5	12.60	0.0295	10.1	17.12	0.0527	10.2	23.00
	16.9	12.85		16.8	17.57		17.3	23.93
	25.0	13.00		25.0	17.99		25.0	24.75
	36.4	12.95		35.8	18.24		35.9	25.50
	45.8	12.77		44.9	18.29		47.7	25.63

The reaction between tin or its chlorides and bromine trifluoride was violent and gave products containing varying amounts of combined bromine trifluoride. The analysis for bromine and fluorine was made as before. Tin was determined iodometrically in hydrochloric acid solution after reduction with aluminium foil in a carbon dioxide atmosphere. Anhydrous stannous chloride, prepared by Stephen's method (*J.*, 1930, 2786), inflamed in contact with liquid bromine trifluoride, but the reaction could be controlled by dilution with bromine. Excess of bromine trifluoride was removed as in the preparation of the antimony compound, but the product did not attain a constant weight, showing that the bromine trifluoride in the compound was less firmly held. This is illustrated by the following experiments, in each of which evacuation was continued for 6 hours. Starting with tin and evacuating at 40° the product

had the composition $\text{SnF}_4 \cdot 0.89\text{BrF}_3$. Starting with stannous chloride and evacuating at 15° it was $\text{SnF}_4 \cdot 1.76\text{BrF}_3$; at 35° , $\text{SnF}_4 \cdot 0.75\text{BrF}_3$, and at 100° , $\text{SnF}_4 \cdot 0.46\text{BrF}_3$. A sample heated for the same time in vacuum at 190° yielded SnF_4 free from bromine.

The white product in these experiments was hygroscopic and turned brown in moist air. It dissolved in water with a slight hissing noise but was insoluble in, and without action on, pyridine or acetone. Ether was ignited. The preparations from tin chlorides contained no chlorine. It is considered that the above products are derived from the dissociation of a stannifluoride $(\text{BrF}_2)_2\text{SnF}_6$ analogous to calcium bromofluoride $\text{Ca}(\text{BrF}_4)_2$, which is also impossible to prepare in a pure state by the process of removing the excess solvent in vacuum.

Conductivity Measurements with Solutions of SbBrF_6 and $\text{SnBr}_2\text{F}_{10}$ in Bromine Trifluoride.—Conductivity measurements made on solutions of antimonous oxide and stannous chloride in bromine trifluoride are summarised in Table III.

Direct current measurements with solutions of antimony trifluoride in bromine trifluoride were made as before. A brown coloration was again produced round the cathode and there was a sharp colour boundary in the tube connecting the two electrode compartments. The liquid round the anode retained its yellow colour. The solutions did not obey Ohm's law, though no sharp break occurred in the current-voltage curves. Typical data for a solution of SbBrF_6 are given below (concn.: 0.042 g.-mol./1000 g.):

Voltage	0.10	0.20	0.30	0.40	0.80	1.20	2.40	3.00	10	30	100
Current (milliamp.)	0.10	0.20	0.32	0.45	0.99	1.59	3.33	4.10	16.2	52.0	198
$10^{-3}v/C$	100	100	94	89	81	75	72	73	62	58	53

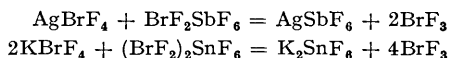
TABLE IV.

Concn. of Sb compound.*	Concn. of Ag compound.*	Ratio.	Temp.	Sp. cond. ($\text{ohm}^{-1}\text{cm.}^{-1} \times 10^3$).	Concn. of Sb compound.*	Concn. of Ag compound.*	Ratio.	Temp.	Sp. cond. ($\text{ohm}^{-1}\text{cm.}^{-1} \times 10^3$).
(a) Titration of AgBrF_4 solution with SbBrF_6 .									
0	0.0367	0	9.9°	12.58	0.0271	0.0368	0.74	10.4°	10.42
			17.0	13.16				17.7	10.74
			25.0	13.70				25.0	11.00
			34.0	14.20				33.8	11.17
			45.7	14.64				45.7	11.30
0.00727	0.0363	0.20	10.5	11.26	0.0513	0.0368	1.40	11.3	14.87
			17.8	11.69				19.0	15.55
			25.0	12.07				25.0	16.02
			33.6	12.39				34.3	16.64
			46.0	12.69				44.7	17.18
0.0227	0.0365	0.62	11.2	10.55	0.0619	0.0366	1.69	9.1	16.55
			17.7	10.91				17.5	17.55
			35.0	11.20				25.0	18.34
			35.4	11.31				34.2	19.10
			44.7	11.43				44.7	19.86
					0.0740	0.365	2.03	10.9	20.98
								17.5	22.01
								25.0	23.22
								35.0	24.50
								44.0	25.59
(b) Titration of KBrF_4 with $\text{SnBr}_2\text{F}_{10}$.									
0	0.0373	0	25.0°	15.05†	0.0298	0.0375	0.79	10.8	10.99
								17.5	11.30
0.0112	0.0371	0.30	10.4	11.35				25.0	11.57
			17.1	11.81				44.1	11.74
			25.0	12.26					
			37.0	12.85	0.0364	0.0372	0.98	10.6	12.90
			47.0	13.15				17.2	13.25
								25.0	13.61
0.0177	0.0374	0.47	10.9	10.39				41.6	13.86
			18.4	10.71					
			25.0	10.93	0.0447	0.0372	1.20	10.7	14.31
			40.5	11.19				18.3	14.82
								25.0	15.16
0.0230	0.0372	0.62	11.0	10.55				44.4	15.54
			17.9	10.87					
			25.0	11.13	0.0589	0.0375	1.57	10.6	17.47
			39.7	11.40				17.5	18.15
								25.0	18.71
								41.3	19.39

* G.-mols./1000 g. of BrF_3 .

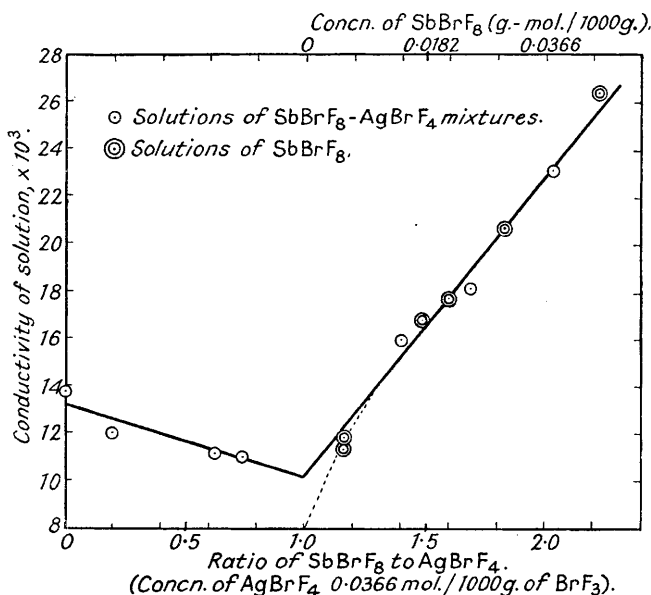
† Interpolated from previous results: Table I.

Conductometric Titration of Acids and Bases in Bromine Trifluoride.—Titrations could not be performed in the usual manner because of the great reactivity of the solvent, which explodes in contact with lubricants and therefore cannot be passed through taps. Solutions were therefore made up by mixing the appropriate amounts of the solids which produce the acid and base on reaction with bromine trifluoride. This mixture was dissolved in bromine trifluoride in a silica flask, and the solution transferred to the conductivity cell as already described. In the first set of determinations a constant amount of silver chloride was used with increasing amounts of antimonous oxide and, in the second, the amount of potassium chloride was fixed while that of stannous chloride varied. In each case the product was soluble in bromine trifluoride. The reactions occurring were



At each concentration observations were made at several temperatures. The data obtained are summarised in Table IV.

These results show that there is a well-defined minimum conductivity for a 1 : 1 ratio of reactants in the titration of the silver base with the antimony acid. In the case of the potassium base and the tin acid this ratio is 2 : 1. It is apparent, therefore, that the tin acid $(\text{BrF}_2)_2\text{SnF}_6$ is effective as such in bromine trifluoride solution even though the compound undergoes decomposition with loss of bromine trifluoride



when its isolation is attempted. The figure shows the marked break in the conductivity in the first experiment. In it a number of points are included, corresponding to the upper horizontal scale, which show the variation of the conductivity of SbBrF_6 with concentration determined in an independent series of experiments (Table III). The fact that these points lie along the right-hand branch of the curve shows that in this region the excess of acid determines the conductivity.

Salt Formation from Acid-Base Reactions in Bromine Trifluoride.—The following experiments were made in order to isolate and characterise as far as possible the salt-like products of the above reactions. Equimolecular proportions of antimony trioxide or trifluoride and the chlorides of potassium or silver were allowed to react with excess of bromine trifluoride. On evaporation of the excess of solvent in vacuum at room temperature the corresponding fluoroantimonate contaminated with a little bromine trifluoride was left.

Silver hexafluoroantimonate obtained from antimony trifluoride (Found: Ag, 31.0; F, 34.1; Br, 0.7. AgSbF_6 requires Ag, 31.4; F, 33.2%) was less pure than that from antimonous oxide (Found: Ag, 31.0; F, 33.6%; Br, nil). An experiment with excess of silver chloride gave the expected mixture of AgSbF_6 and AgBrF_4 . Barium chloride with two equivalents of antimony trifluoride gave a product containing bromine trifluoride [Found: Ba, 20.1; Sb, 36.0; F, 35.9; Br, 4.0%; equiv., 672. Calc. for $\text{Ba}(\text{SbF}_6)_2 \cdot 0.46\text{BrF}_3$; Ba, 20.5; Sb, 36.2; F, 37.9; Br, 5.4%; equiv., 672]. It has not yet been possible to determine whether in this and in similar cases the product obtained contains "bromine trifluoride of crystallisation."

Equimolecular proportions of stannous and barium chlorides gave a product which was free from bromine, and insoluble in bromine trifluoride and also in cold water (Found: Sn, 31.5%; equiv., 365. Calc. for BaSnF_6 ; Sn, 32.1%; equiv., 370). Products containing excess of bromine trifluoride were obtained from stannous chloride and silver chloride (Found: Ag, 44.8; F, 24.2; Br, 3.4%; equiv., 488. Calc. for $\text{Ag}_2\text{SnF}_6 \cdot 0.27\text{BrF}_3$; Ag, 44.8; F, 23.4; Br, 4.1%; equiv., 488). A similar result was obtained

with potassium chloride and stannous chloride (Found : Sn, 25.5; Br, 18.1%; equiv., 470. Calc. for $K_2SnF_6 \cdot 1.15BrF_3$: Sn, 25.3; Br, 19.7%; equiv., 470).

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