454. *The Formation of Complex Fluorides. Part I. The Relation between the Conductivities of Boric, Arsenious, and Antimonic Fluorides and Complex Formation.*

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The formation of alkali complex fluorides by addition and neutralization reactions in non-aqueous solutions is discussed in relation to the conductivity of the fluorides used as solvents. The specific conductivities of boron trifluoride, arsenic trifluoride, and antimony pentafluoride are $<5 \times 10^{-10}$ (at $-120°$), $2 \cdot 4 \times 10^{-5}$ (at $25°$), and $1 \cdot 2 \times 10^{-8}$ (at $25°$) ohm^{-1} cm.$^{-1}$ respectively. The possible ionic nature of the double fluorides formed by Group-VB and -VIIB fluorides, including the new compounds AsF$_3$,SbF$_5$ and IF$_5$,SbF$_5$, is mentioned, and the viscosities of arsenic trifluoride and antimony pentafluoride are reported.

COMPLEX fluorides of the alkali and alkaline-earth metals can be prepared either by gas–solid reactions or by reactions in solution. The former, because of their high activation energies, are carried out at high temperatures and sometimes at high pressures and consequently are only applicable to the thermally stable complexes. The combination of sodium fluoride with boron

trifluoride, for example, although noticeable at room temperature, is quantitative at 400° (De Boer and van Liempt, *Rec. Trav. chim.*, 1927, **46**, 124). Similarly, potassium fluoride and uranium hexafluoride combine in equimolecular proportions at 200° under 70 atmospheres' pressure (Martin and Albers, *Naturwiss.*, 1946, **33**, 370). Direct fluorination is an alternative gas–solid reaction which has been used to produce a salt-like product (presumably $NaOsF_9$) from sodium fluoride and osmium (Ruff and Tschirch, *Ber.*, 1913, **46**, 929). Klemm and Huss (*Z. anorg. Chem.*, 1949, **258**, 221) have recently used similar reactions to prepare K_3CoF_7, K_2NiF_6, and K_3CuF_6 from mixtures of the corresponding chlorides.

Reactions in solution can occur at much lower temperatures since in these reactions less energy is required to disrupt the crystal lattice than is required in non-solvent reactions because of the partial compensation provided by the solvation energy. Anhydrous and aqueous hydrogen fluoride are the common solvents, and bromine trifluoride has recently been used to prepare a wide range of complex fluorides (Woolf and Eméleus, *J.*, 1950, 1050).

There appears to be a relation between complex formation in solution and the electrical conductivity of the anion component fluoride. The conductivities of the " covalent " fluorides so far examined fall into two groups. The fluorides of the first group have conductivities of at least 10^{-5}ohm^{-1} cm.$^{-1}$, and it is these fluorides which form complexes with the alkali fluorides in solution. Thus arsenic trifluoride, bromine trifluoride, iodine pentafluoride, and hydrogen fluoride, which with potassium fluoride form $KAsF_4$, $KBrF_4$, KIF_6, and KHF_2 respectively, have conductivities of $2 \cdot 4 \times 10^{-5}$ (at 25°), $8 \cdot 0 \times 10^{-3}$ (at 25°), 2—3 $\times 10^{-5}$ (at 25°), and $1 \cdot 4 \times 10^{-5}$ (at — 15°) (Sharpe and Eméleus, *J.*, 1948, 2135; Eméleus and Sharpe, *J.* 1949, 2206; Banks, Eméleus, and Woolf, *J.*, 1949, 2861; Fredenhagen and Cadenbach, *Z. anorg. Chem.*, 1929, **178**, 289).

In the liquid state the second group of fluorides, with conductivities below 10^{-5}ohm^{-1} cm.$^{-1}$, do not react at an appreciable rate with alkali fluorides. This group comprises boron trifluoride ($\kappa < 5 \times 10^{-10}$ohm^{-1} cm.$^{-1}$ at — 120°), antimony pentafluoride ($\kappa = 1 \cdot 2 \times 10^{-8}$ohm^{-1} cm.$^{-1}$ at 25°), and chlorine trifluoride ($\kappa = 3 \times 10^{-9}$ohm^{-1} cm.$^{-1}$ at 0°; Banks, unpublished).

Reactions which lead to complex-fluoride formation have been demonstrated in bromine trifluoride between compounds containing anions and cations characteristic of the solvent, *e.g.*,

$$K^+BrF_4^- + BrF_2^+SbF_6^- = KSbF_6 + 2BrF_3$$
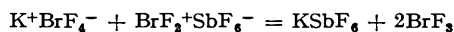
(Woolf and Eméleus, *J.*, 1949, 2865). These reactions are analogous to neutralization in aqueous solution. It is now found that neutralizations also occur when other members of the first group of fluorides are used as solvent. The conductivity of arsenic trifluoride, for example, is greatly increased by small amounts of potassium or antimonic fluorides, and the compounds KF,AsF_3 and SbF_5,AsF_3 can be isolated from the respective solutions. Equimolecular mixtures of these two compounds in arsenic trifluoride form the complex fluoroantimonate which can be isolated by removal of the solvent *in vacuo*, in agreement with a neutralization equation :

$$K^+AsF_4^- + AsF_2^+SbF_6^- = KSbF_6 + 2AsF_3$$

If no interaction had occurred, a residue of $KAsF_4$ would have remained, since this compound, unlike $SbAsF_8$, is non-volatile *in vacuo*. In addition, although no solid compound could be isolated from boron trifluoride and arsenic trifluoride, the former increased the conductivity of the latter to a small extent and, when it was passed into a solution of potassium fluoride in arsenic trifluoride, potassium tetrafluoroborate was produced. Again, the preparation may be regarded as taking place between potassium tetrafluoroarsenite and an unstable compound $AsF_2^+BF_4^-$ in solution. Similar intermediates have been postulated to explain the formation of hexafluorophosphates in bromine trifluoride solution (Eméleus and Woolf, *J.*, 1950, 164).

Preliminary investigations indicate that iodine pentafluoride behaves in an analogous fashion, since addition of potassium fluoride enhances its conductivity and a compound IF_5,SbF_5 can be prepared in the same manner as the corresponding arsenic compound described above. Finally, although no examples of neutralization reactions in liquid hydrogen fluoride have been reported, it seems probable that potassium hydrogen fluoride would react with the compound $H_2F^+BF_4^-$ (Hantzsch, *Ber.*, 1930, **63**, 1789) in anhydrous hydrogen fluoride to produce potassium fluoroborate.

The structures of the compounds formed between the fluorides of Groups VB and VIIB require further investigation. The compounds BrF_3,SbF_5, IF_5,SbF_5, AsF_3,SbF_5, $(SbF_3)_2,SbF_5$, and $(SbF_3)_5,SbF_5$ have so far been prepared, but the number of such complexes is, in all probability, not limited to these examples. In particular, the compounds $(SbF_3)_2,SbF_5$ and $(SbF_3)_5,SbF_5$ should be re-examined in view of the present work, since $(SbF_3)_2,SbF_5$ (Ruff and

Plato, *Ber.*, 1904, **37**, 678), for example, may well be a salt $(SbF_4)_2,SbF_7$. The anion of this hypothetical salt may be present in the corresponding potassium compound $K_2SbF_7,2H_2O$ (Marignac, *Annalen*, 1868, **145**, 237). It is improbable, however, that all the double fluorides of these groups will be ionic in the solid state, although many may ionize in solution owing to the effect of solvation in altering the type of bonding.

Some observations on viscosities made during the course of this work are of interest. Arsenic trifluoride is about as viscous as water and has a viscosity $\eta = 1.17$ centipoises at 8·3°. The plot of log η against the reciprocal of the absolute temperature is linear over the limited range examined (−5° to +10°), and this leads to an activation energy for viscous flow of 2·41 kcals. mole^{-1}, which is approximately a quarter of the latent heat of vaporization of the liquid, 8·57 kcals. mole^{-1} (Russell, Rundle, and Yost, *J. Amer. Chem. Soc.*, 1941, **63**, 2825). This is in agreement with the theory of absolute reaction rates (Kincaid, Eyring, and Stearn, *Chem. Reviews*, 1941, **28**, 301). Antimony pentafluoride in contrast, has a viscosity of 460 centipoises at 20°, which is of the same order as that of glycerol. The temperature variation of the viscosity has not been examined over a sufficiently wide range to decide whether it is an important factor in determining the rapid variation of electrical conductivity with temperature; between 20° and 90° the conductivity increases a hundred-fold, and the corresponding activation energy for the conduction process is 14·3 kcals. mole^{-1}, a value which is considerably higher than the usual values for this quantity. There are, as yet, insufficient data for one to draw any reliable comparison between the physical properties of the corresponding fluorides of Groups VB and VIIB.

<div align="center">EXPERIMENTAL.</div>

Arsenic Trifluoride.—Moissan observed that arsenic trifluoride was a poor conductor whose conductivity was raised by addition of potassium fluoride. No fluorine was evolved on electrolysis, but the solvent was attacked with the formation of arsenic pentafluoride at the anode, and deposition of arsenic at the cathode, phenomena similar to those observed during the electrolysis of bromine trifluoride.

Arsenic trifluoride was prepared by the action of concentrated sulphuric acid (250 c.c.) on a well-dried, intimate mixture of arsenious oxide (100 g.) and calcium fluoride (120 g.) in a Pyrex-glass apparatus. The product was purified by refluxing it over sodium fluoride and fractionating it through a short Fenske column. It was found, in agreement with Russell, Rundle, and Yost (*loc. cit.*), that specimens so prepared were without action on glass and had a b. p. several degrees lower than that reported by previous workers. The present investigation gave as the b. p. 57·8°/760 mm., a value which altered by 0·03$_8$° per mm. The product had $n_D^{17·5}$ 1·362 and $d_4^t = 2·6605 - 0·00370t$ in the range 5—25°.

Specific electrical conductivity was measured at 1000 cycles A.C., with an apparatus described by Haszeldine and Woolf (*J. Soc. Chem. Ind.*, in the press). The design of the conductivity cell is shown in the Figure. It consisted of a silica vessel, connected by means of a ground joint to a soft-glass electrode holder which also served to seal the apparatus. The electrodes were of platinum and, when the cell was in use, only a small section of the soft-glass holder was in contact with the liquid under investigation. The arsenic trifluoride, after two distillations from sodium fluoride at atmospheric pressure, had a conductivity of $5·29 \times 10^{-5}$ohm^{-1} cm.$^{-1}$ at 25° and a linear temperature dependence of conductivity (+1·05 × 10^{-6}ohm^{-1} cm.$^{-1}$ deg.$^{-1}$). There was no indication of attack of arsenic trifluoride on the cell, the value of the conductivity remaining constant during 2 hours.

The D.C. resistance was not ohmic, and initially no current flowed below an applied potential of 1·5 v. This value, however, was not reproducible since electrolysis increased the conductivity of the liquid irreversibly; at the end of the experiment the A.C. conductivity had risen to $12·9 \times 10^{-5}$ohm^{-1} cm.$^{-1}$ at 25°.

Two freshly prepared samples of arsenic trifluoride were distilled from sodium fluoride and then twice fractionated *in vacuo*. The middle fractions were vacuum-distilled into the cell. The values obtained for the conductivity are given in Table I. It may be seen that, at 25°, the conductivity of arsenic trifluoride is $2·28—2·50 \times 10^{-5}$ohm^{-1} cm.$^{-1}$ with a relative temperature coefficient $\left(\frac{1}{\kappa}\cdot\frac{d\kappa}{dt}\right)_{25°} = 10\%$.

<div align="center">TABLE I.</div>

<div align="center">*Conductivity of arsenic trifluoride from 0° to 40°.*</div>

Specimen I		Specimen II.	
Temp.	$\kappa \times 10^5$,ohm^{-1} cm.$^{-1}$.	Temp.	$\kappa \times 10^5$,ohm^{-1} cm.$^{-1}$.
4·0°	1·83	−0·7°	1·81
11·8	2·01	8·6	2·08
19·6	2·18	14·8	2·22
25·0	2·28	18·9	2·31
29·7	2·40	25·0	2·50
37·8	2·56	29·2	2·61
$d\kappa/dt = 2·1_6 \times 10^{-6}/°$ c.		$d\kappa/dt = 2·6_7 \times 10^{-6}/°$ c.	

The kinematic viscosity (ν) of arsenic trifluoride was measured using a modified Ostwald U-tube viscometer with a capillary diameter of 0·60 mm., in accordance with British Standard 188 : 1937. The viscometer was filled directly, and moisture was excluded by means of liquid-air traps. The results are contained in Table II, which also gives values of the dynamic viscosity, $\eta = \nu \cdot d_4^t$.

Boron Trifluoride.—Commercial boron trifluoride, supplied by courtesy of Imperial Smelting Corporation Ltd., was condensed into the conductivity cell (Fig.) at $-120°$ and a D.C. potential of 110 v. applied. No current was detected with a microammeter, which places an upper limit of 5×10^{-10}ohm^{-1} cm.$^{-1}$ on the conductivity of liquid boron trifluoride.

Antimony Pentafluoride.—Antimony pentafluoride was prepared by passing fluorine over molten antimony trifluoride, previously dried at 120°, and maintained a little above its m. p. (292°) in an electrically heated nickel reaction vessel. The antimony pentafluoride which distilled was purified by vacuum-distillation. The colourless liquid, m. p. 7·0°, was free from tervalent antimony, and was transferred, *in vacuo*, to a soft-glass conductivity cell of a type already described (Greenwood and Eméleus, *J.*, 1950, 987), which was then vacuum-sealed. As the conductivity was below the limit of sensitivity of the A.C. bridge circuits, the current flowing through the cell under an applied D.C. potential of 24 v. was measured by means of a sensitive galvanometer. This procedure was admissible since the resistance was ohmic (Table III), and there was no evidence of any decomposition potential. The specific conductivity of antimony pentafluoride, measured in this way over the range 5—90°, is given in Table IV. The value at room temperature showed no change during one day.

Conductivity cell.

The kinematic viscosity (ν) of antimony pentafluoride was measured, with a British Standard U-tube visometer with a capillary diameter of 1·15 mm. This viscometer was incorporated in the vacuum-distillation apparatus to facilitate transfer of antimony pentafluoride under anhydrous conditions. After the level of the liquid in the viscometer had been adjusted to the correct height, dry air was admitted through liquid-air traps by a suitable arrangement of taps, and the time of efflux measured. The results so obtained are summarized in Table V. According to Ruff and Plato (*Ber.*, 1904, **37**, 673), antimony pentafluoride has $d_4^{22.7}$ 2·993. This would give a dynamic viscosity of $\eta \simeq 460$ centipoises at 20°.
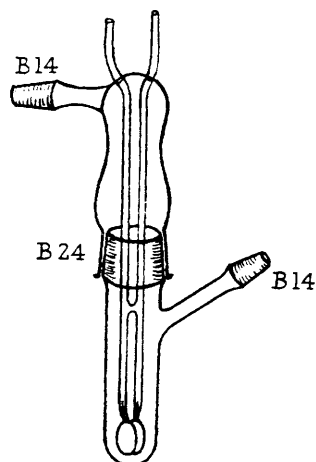
TABLE II.

Viscosity of arsenic trifluoride from $-5°$ to $+10°$.

Temp.	$-4\cdot5°$	$+0\cdot8°$	$+8\cdot3°$
ν, centistoke	0·543	0·500	0·444
η, centipoises	1·15$_3$	1·32$_9$	1·16$_8$

TABLE III.

Current–voltage relation for antimony pentafluoride at 90°.

Volts (v.).	Amps. $\times 10^6$ (I).	$(v/I) \times 10^{-6}$.	Volts.	Amps. $\times 10^6$.	$(v/I) \times 10^{-6}$.
0·3	0·095	3·2	2·4	0·833	2·9
0·6	0·191	3·1	2·8	0·981	2·9
0·9	0·306	2·9	3·25	1·13	2·9
1·2	0·407	3·0	4·0	1·39	2·9
1·6	0·547	2·9	4·5	1·56	2·9
2·0	0·699	2·9	5·5	1·92	3·0

TABLE IV.

D.C. Conductivity of antimony pentafluoride from 5° to 90°.

Temp.	$\kappa \times 10^9$,ohm^{-1} cm.$^{-1}$.	Temp.	$\kappa \times 10^9$,ohm^{-1} cm.$^{-1}$.	Temp.	$\kappa \times 10^9$,ohm^{-1} cm.$^{-1}$.
6·0°	4·37	50·0°	58·5	76·4°	335
17·4	7·65	55·5	105	79·6	395
24·4	11·5	59·8	134	85·6	830
35·5	22·5	65·0	188	89·5	975
45·0	42·6	69·5	251		

TABLE V.

Viscosity of antimony pentafluoride from 0° to 20°.

Temp.	2·2°	12·0°	20·0°
ν, centistokes	246	183	154

Preparation of KAsF$_4$.—In a series of experiments weighed amounts of well-dried potassium fluoride were refluxed with varying amounts of arsenic trifluoride with the exclusion of moisture. Most of the solvent was removed at atmospheric pressure, and the remainder *in vacuo.* The solubility of potassium fluoride was small but complete dissolution of 0·3 g. in 60 c.c. of arsenic trifluoride was obtained after 45 minutes' refluxing. The residue attained constant weight after 5 hours *in vacuo* at room temperature. It was analysed by dissolution in cold sodium hydroxide solution, arsenic being determined iodometrically and fluorine by the Willard–Winter method after distillation from 50% sulphuric acid (Found : As, 39·3; F, 39·1%; equiv., 190. KAsF$_4$ requires As, 39·3; F, 40·0%; equiv., 190). When the potassium fluoride did not dissolve completely the composition of the products varied and they were probably mixtures of KF and KAsF$_4$. The stability of the *compound* was illustrated in some of these experiments by the retention of appreciable quantities of arsenic trifluoride at temperatures up to 100° *in vacuo.*

Preparation of AsF$_3$,SbF$_5$.—Ruff, Graf, Heller, and Knoch (*Ber.,* 1906, **39**, 4316) observed a white precipitate on mixing arsenic trifluoride with either an equimolecular quantity or an excess of antimony pentafluoride. They suggested that the trifluoride was fluorinated to the pentafluoride which then formed a compound with antimony trifluoride or pentafluoride. It is shown below that the arsenic remains tervalent in a 1 : 1 compound with antimony pentafluoride.

Antimony pentafluoride (2·9 g.) was vacuum-distilled into a silica flask and an approximately equimolecular amount of arsenic trifluoride added (0·68 c.c.). Heat was evolved and a crystalline solid separated. The latter was volatile in a high vacuum, and the bulk of the material in the flask was removed in this way. The solid residue (0·9 g.) was analysed for tervalent antimony and fluorine as described above. In order to determine arsenic and antimony together the former was oxidised to the quinquevalent state with aqueous sodium peroxide and was precipitated and weighed as the penta-sulphide after passage of hydrogen sulphide through the solution rendered strongly acid with hydro-chloric acid. The antimony in the filtrate was precipitated after dilution and further passage of hydrogen sulphide, the precipitate being converted into the trisulphide by heating it at 280° in a current of oxygen-free nitrogen (Found : As^{III}, 21·1; Sb, 34·8; F, 43·9; Total As, 21·5. AsF$_3$,SbF$_5$ requires As^{III}, 21·5; Sb, 34·9; F, 43·6; Total As, 21·5%).

Antimony pentafluoride was converted quantitatively into the *compound* AsF$_3$,SbF$_5$ by treatment with a two-fold excess of the trifluoride. The solid crystallised out at 0° and after evacuation for 2 hours at 30 mm. pressure the weight became constant (Found : As^{III}, 21·3; Sb, 34·3%; equiv., 346. AsF$_3$,SbF$_5$ requires As^{III}, 21·5; Sb, 34·9%; equiv., 349).

The absence of tervalent and the presence of quinquevalent antimony was shown by qualitative tests with cupferron and rhodamine-B respectively in aqueous solution, thus disposing of the possible structure AsF$_5$,SbF$_3$.

Complex Formation in Arsenic Trifluoride.—*Potassium hexafluoroantimonate.* A slight excess of antimony pentafluoride (1·07 moles) was washed into a flask containing potassium fluoride, by means of arsenic trifluoride, and, after refluxing, the excess solvent was removed as previously described. The residue contained only 2% of arsenic and had an equivalent weight of 267 after 2 hours *in vacuo* (KSbF$_6$ = 275). In a second experiment, with a ratio SbF$_5$/KF of 1·67, the residue contained 0·9% of arsenic.

Potassium tetrafluoroborate. Boron trifluoride was bubbled, in the cold, through 15 c.c. of arsenic trifluoride containing about 0·3 g. of potassium fluoride, and the residue, after partial removal of the solvent at room temperature, was heated to 180° to remove all traces of arsenic trifluoride. This eliminated the necessity of analysing mixtures of KAsF$_4$ and KBF$_4$. The residue was analysed by precipitating nitron fluoroborate and consisted of KBF$_4$ 80% and KF 20%. The nitron precipitate was identified by analysis (Found : C, 59·9; H, 4·5; N, 14·2. Calc. for C$_{20}$H$_{17}$N$_4$F$_4$B : C, 60·0; H, 4·3; N, 14·0%).

In contrast to this experiment in the presence of arsenic trifluoride, 0·2 g. of potassium fluoride was recovered unchanged after being refluxed at −95° with 20 c.c. of boron trifluoride alone. The condenser was maintained at −112° by means of solid carbon disulphide.

Conductivity of Solutions in Arsenic Trifluoride.—Addition of 0·15 g.-mol. of potassium fluoride per 1000 g. of arsenic trifluoride increased the conductivity of the latter from 2·5 × 10^{-5} to 3·2 × 10^{-3}ohm^{-1} cm.$^{-1}$ at 25°, without all the potassium fluoride going into solution. Similarly 0·135 g.-mol. of antimony pentafluoride per 1000 g. increased the conductivity to 1·03 × 10^{-2} at 25°. The fuming liquid which resulted when boron trifluoride was passed through arsenic trifluoride had a conductivity of 8·4 × 10^{-5} compared with the initial value of 3·7 × 10^{-5}ohm^{-1} cm.$^{-1}$ for the sample of arsenic trifluoride used.