Fluorosulphonic Acid. Part II. Ionization in the Anhydrous Solvent and the Formation of Complex Fluorides.*

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The preparation of complex fluorides, by means of solvents, between component fluorides close together in the periodic classification is discussed. Fluorosulphonic acid is considered as a possible solvent. Its main self-ionization, which gives rise to a conductivity between that of anhydrous hydrofluoric and sulphuric acids, is to a solvated proton and the fluorosulphonate ion. The ions HSO_3^+, H_2F^+, and $S_2O_6F^-$ are considered to be present in negligible amounts. Fluorides soluble in fluorosulphonic acid enhance the conductivity. The alkali fluorides, which form fluorosulphonates by elimination of hydrogen fluoride, are the bases in this system. Antimony pentafluoride, which contains an antimony anion in fluorosulphonic acid solution, is believed to form hexafluoroantimonic acid by elimination of sulphur trioxide. This is regarded as an acid and indeed can be neutralized with potassium fluorosulphonate solution to give a conductometric minimum at approximately equimolecular proportions. Solutions of other fluorides are then classified as acids or bases with reference to potassium fluorosulphonate or antimony pentafluoride in conductometric titrations. AuF_3, TaF_5, and PtF_4 are acids: AsF_3, SbF_3, BrF_3, and IF_5 are bases. The proton acid $HClO_4$ appears not to behave as an acid in the fluorosulphonic acid system. Organic compounds can function as bases, and both pyridine and nitrobenzene have been titrated with antimony pentafluoride.

THE limitations imposed by solvents in the preparation of complex fluorides have been mentioned in Part I *. When the component fluorides are widely separated in the periodic classification the practical limits to preparation of solvent-free complexes are imposed by sparing solubilities of fluorides, and further reaction with the solvent after solution. The most serious of the latter effects, apart from solvation of cation or anion, is solvolysis, a reversal of the neutralization type of reaction. Solvolysis in bromine trifluoride is typical and has been discussed by Sharpe (*J.*, 1950, 2907, 3444). It is intimately connected with the difference in acid and base strengths as well as their absolute magnitude. (In the formation of complex fluorides it is considered that the component fluorides react with the solvent to form acids or bases which contain cations or anions, respectively, characteristic of the solvent. The acids are neutralized by bases to give the complexes. In fluoride solvents an alternative description of the initial process is that the acid is a fluoride-ion acceptor, the base a fluoride donor. It is in these senses that the terms acid and base are used.) The way to eliminate solvolysis is therefore by adjustment of acid and base strengths and this is only possible if a sufficient range of solvents or solvent mixtures is available.

When the component fluorides are close in the periodic classification the difficulties are accentuated on account of the smaller difference in properties between the acid and base components. The high electronegativity of fluorine, however, should permit the closest approach for any of the halides or pseudo-halides. This would occur between halides in the same group or even between halides of the same element in different valency states. The preparation of double fluorides of group V elements is of interest for valency theory, and serves to demonstrate the difficulties. With bromine trifluoride only the pentafluorides can form solutions, and these behave as acids. When pairs of fluorides are mixed, only the corresponding pairs of acids can be isolated. A solvent is required which is not oxidising and has an acid strength between the strengths of the fluoride components of a complex. One possibility is to use a fluoride of group V itself as the solvent.

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* Part I, *J.*, 1954, 2840.

Arsenic trifluoride has been used to prepare an approximately equimolar compound of antimony tri- and penta-fluorides, the missing member of the series prepared by Ruff and Plato (*Ber.*, 1904, **37**, 673). The uses of antimony trifluoride and selenium tetrafluoride as solvents are obvious extensions. However, it is doubtful whether these solvents will have any general application and it is for this reason that fluorosulphonic acid has been studied.

Little is known of its solvent or acid properties. In Part I (*loc. cit.*) it was shown to differ from sulphuric acid in being a true compound and not a constant-boiling mixture, and in dilute aqueous solution it ionizes to hydroxonium and fluorosulphonate ions. The anhydrous acid has a conductivity of $2{\cdot}20 \times 10^{-4}$ mho at 25°, intermediate between those of sulphuric and hydrofluoric acids. (Gillespie and Wasif, *J.*, 1953, 203, give $1{\cdot}03 \times 10^{-2}$ at 25° for sulphuric acid; Fredenhagen and Cadenbach, *Z. anorg. Chem.*, 1928, **178**, 289, give $1{\cdot}4 \times 10^{-5}$ at $-15°$ for hydrogen fluoride.) The conductivity varies exponentially with temperature between $-78°$ and 58°, and in common with certain other fluorides the ratio of the activation energies of viscous flow and conduction is less than unity (Fairbrother, Frith, and Woolf, *J.*, 1954, 1031). The conductivity can be explained by self dissociation but a choice of equilibria, which may not be mutually exclusive, is possible. For simplicity the unsolvated fluoride and hydrogen ions are given in the following schemes instead of the more likely $HSO_3F_2^-$ and $H_2SO_3F^+$ ions :

$$HSO_3F \rightleftharpoons H^+ + SO_3F^- \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

$$HSO_3F \rightleftharpoons HSO_3^+ + F^- \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

$$2HSO_3F \rightleftharpoons H_2F^+ + S_2O_6F^- \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

The evidence shows that the first ionization is the predominant one. The only gas produced on electrolysis of the anhydrous acid is hydrogen at the cathode. In the initial stages 0·5 mole of gas is liberated for each Faraday of electricity. This is compatible with (1) or (3) but not (2), since the fluoride ion would need to discharge as fluorine. The transport of fluorine to the anode renders (3) improbable, since the relative mobility of the ions would tend to transport it in the opposite direction. In favour of (1) are the facts that (i) the molecular conductivity of potassium fluorosulphonate solutions is practically independent of dilution when the solvent conductivity is deducted; (ii) the solvent becomes oxidising at the anode during electrolysis and, for example, tervalent is converted into quinquevalent antimony. The former (i) is analogous to the behaviour of bisulphates in anhydrous sulphuric acid (Hantzsch, *Z. phys. Chem.*, 1907, **61**, 257) and a similar repression of solvent ionization, by the fluorosulphonate ion of the salt, is indicated. The latter (ii) is in accord with the formation of an oxidising perdifluorosulphonate ion: $2SO_3F^- - e^- \longrightarrow S_2O_6F_2^-$. The other ionizations may occur to a minor extent. The presence of HSO_3^+ would explain the sulphonation of benzene (Meyer and Schramm, *Z. anorg. Chem.*, 1932, **206**, 24) and such an ion has been postulated to explain sulphonations in oleum (Brand and Horning, *J.*, 1952, 3922). The existence of the ions of equilibrium (3) is less certain. The $S_2O_6F^-$ ion has been reported only recently in an unstable potassium salt formed from sulphur trioxide and potassium fluorosulphonate (Lehmann and Kolditz, *ibid.*, 1953, **272**, 69), but there is no evidence from conductivity data of a second acid in the HF–SO_3 system. The conductivity decreases steadily from a maximum at HF,SO_3 through the composition $HF,2SO_3$.

The evidence for the H_2F^+ ion was based on the work of Hantzsch (*Ber.*, 1930, **63**, 1789) who claimed to have prepared the crystalline tetrafluoroborate and perchlorate by mixing hydrogen fluoride with boron fluoride and perchloric acid respectively. These compounds were solids whose m. p.s were well above those of the components. By analogy with his previous work on nitric acid–perchloric acid mixtures he assigned them ionic structures. His results have been controverted in recent years, for the compound $H_2NO_3^+ClO_4^-$ appears to have been a mixture of nitronium and hydroxonium perchlorates contaminated with nitric acid (Goddard, Hughes, and Ingold, *J.*, 1950, 2559), and $H_2F^+ClO_4^-$ appears equally fictitious, since Brauer and Distler (*Z. anorg. Chem.*, 1954, **275**, 157) failed to isolate any appreciable solid, apart from traces of hydroxonium perchlorate due to unavoidable moisture, when hydrogen fluoride was mixed with perchloric acid. The entity of the compound $H_2F^+BF_4^-$ is disproved by the observations of McCauley and Lien (*J. Amer. Chem. Soc.*, 1951, **73**, 2013) who showed that there was no appreciable interaction of boron trifluoride and hydrogen fluoride except in the presence of basic hydrocarbons. Lange disputed the ionization $HSO_3F + H_2SO_4 \rightleftharpoons H_2F^+ + HS_2O_7^-$ because no pyrosulphate ions can be detected (Simons, "Fluorine Chemistry," Academic Press Inc., N.Y., 1950, Vol. I, p. 169). Finally, the boron trifluoride dihydrate, once formulated as $H_2F^+BF_2(OH)_2^-$ (Sowa, Kroeger, and Nieuwland, *J. Amer. Chem. Soc.*, 1935, **57**, 454) by analogy with Hantzsch's $H_2F^+BF_4^-$, has been shown by electrolytic transport in the melt and by conductivity data in solution, to be $H_3O^+BF_3{\cdot}OH^-$ (Greenwood and Martin, *J.*, 1951, 1915; Wamser, *J. Amer. Chem. Soc.*, 1951, **73**, 409). Although there is no longer any evidence for the existence of H_2F^+ in the solid state or in aqueous solution, there is some evidence, from the formation of complex fluorides by neutralization reactions in hydrogen fluoride (Woolf, *J.*, 1950, 3678) and from transport experiments in fluorosulphonic acid, for the existence of equilibrium amounts of this ion. Hydrogen fluoride is readily soluble in fluorosulphonic acid, more than an equimolecular amount being absorbed without evolution of much heat. The solutions, which contain free hydrogen fluoride as indicated by their high vapour tension and attack on silicate glass, are completely separable on distillation. Electrolysis, which causes a net transport of fluorine to the cathode compared with anodic transport of the solvent, shows a positive ion containing the elements. However, it is concluded that the amount of ionization of fluorosulphonic acid to H_2F^+, HSO_3^+, or $S_2O_6F^-$ can only be minute.

The behaviour of proton acids in fluorosulphonic acid depends primarily on their acid strength. There can be few acids able to donate protons to fluorosulphonic acid if it is as strong as indicated in aqueous solution (Part I). Sulphuric acid may be such an acid but the multiplicity of possibilities hampers interpretation ($H_2SO_4 + HSO_3F \rightleftharpoons H_2SO_3F^+ + HSO_4^-$ or $H_3O^+ + S_2O_6F^-$ or $H_2F^+ + HS_2O_7^-$ or $H_3SO_4^+ + SO_3F^-$). It has been shown that sulphuric acid forms solutions about as conducting as those of potassium fluorosulphate but for which the molecular conductivity varies with dilution. Perchloric acid has also been examined briefly and the results described below indicate that its proton is not donated to fluorosulphonic acid.

Fluorides can be qualitatively divided into three groups according to their solubility in fluorosulphonic acid: *viz.*, soluble, KF, AgF, AuF_3, AsF_3, SbF_5, TaF_5, BrF_3, and IF_5; sparingly soluble, BF_3, SnF_4, SbF_3, and PtF_4; and insoluble, BiF_3 and TlF_3. The soluble or sparingly soluble fluorides enhance the conductivity of fluorosulphonic acid. The alkali fluorides dissolve with evolution of heat, elimination of hydrogen fluoride, and formation of fluorosulphonates (Traube, Horenz, and Wunderlich, *Ber.*, 1919, **52**, 1272). Potassium fluorosulphonate is a strong electrolyte in fluorosulphonic acid, the molecular conductivity of these solutions (*ca.* 240) being about double the values attained in the less viscous solvents, bromine trifluoride and water. Thus the ions have an abnormal mobility in fluorosulphonic acid and there is a similarity with solutions of bisulphates in sulphuric acid and alkali fluorides in hydrogen fluoride. It is probable that the abnormal mobility of the fluorosulphonate ion results from a charge transfer of the Grotthus chain type. The metal fluorosulphonates are bases in the fluorosulphonic acid solvent system.

Antimony pentafluoride is readily soluble in fluorosulphonic acid without any evolution of hydrogen fluoride. Its molecular conductivity, corrected for solvent conductivity, varies with dilution. At infinite dilution it is about half that of potassium fluorosulphonate. The antimony is present as an anion because electrolysis of its solution transports antimony to the anode. When antimony pentahalides are dissolved in other solvents (ICl, $AsCl_3$, $POCl_3$, $SOCl_2$, CNCl, HF, AsF_3, BrF_3, IF_5), the antimony is invariably found in complex anions.

If the self-ionization of fluorosulphonic acid to H^+ and SO_3F^- is accepted, there are only two reasonable ionizations for antimony pentafluoride

$$SbF_5 + HSO_3F \rightleftharpoons H^+ + SbF_5SO_3F^- \quad \text{or} \quad H^+ + SbF_6^- + SO_3$$

The latter is preferred because abnormal co-ordinations are required in the first alternative: the ion $SbF_5SO_3F^-$ would require five-fold co-ordination of sulphur, and $SbF_6SO_3^-$ would require seven-fold co-ordination of antimony, but neither type of co-ordination has been previously encountered. The presence of free sulphur trioxide is compatible with the lower conductivity of antimony pentafluoride solutions than of potassium fluorosulphonate solutions. The decrease of solvent conductivity on addition of sulphur trioxide has been mentioned previously. It is recognized that the choice of ionizations is somewhat arbitrary, but the experimental results are most readily explained if potassium fluoride and antimony pentafluoride form a base and an acid by respective displacement of hydrogen fluoride and sulphur trioxide from the solvent.

Neutralization of antimony pentafluoride solution with potassium fluoride solution has been followed conductometrically. The conductivity of an antimony pentafluoride solution falls sharply on the initial additions of the more conducting potassium fluorosulphonate solution, and rises only after the addition of about an equimolar amount of the fluorosulphonate. An excellent end-point is obtained with pyridinium fluorosulphonate, and this salt has been titrated in the reverse manner by addition of the pentafluoride. A cusp-like conductivity curve yields an end-point close to equimolecular proportions. Nitrobenzene forms a yellow solution in fluorosulphonic acid which also produces a sharp end-point when titrated with antimony pentafluoride. The pyridine and nitrobenzene bases have approximately the same molecular conductivities as potassium fluorosulphonate. (The approximate values without solvent correction are 239 at a concentration of 0·080 mole/1000 g. of solvent, 230 at 0·049 and 248 at 0·044, respectively.) This is analogous to the behaviour of bisulphates in sulphuric acid and illustrates again the abnormal mobility of the fluorosulphonate ion. These titrations can all be represented as neutralization reactions of the type $R^+SO_3F^- + H^+SbF_6^- \longrightarrow R^+SbF_6^- + HSO_3F$. The cation formed from nitrobenzene, $C_6H_5{\cdot}NO_2H^+$, has been found in sulphuric acid solutions where its identity has been established by cryoscopic and spectrometric measurements (Gillespie, *J.*, 1950, 2542; Brand, Horning, and Thornley, *ibid.*, pp. 997, 1374).

Other fluorides can be classified as acids or bases by examination of their behaviour with potassium fluorosulphonate or antimony pentafluoride in conductometric titrations, together with transport studies. Auric fluoride is readily soluble in fluorosulphonic acid, the solution having a yellow-orange colour like that of aqueous solutions of chloroauric acid. On titration with antimony pentafluoride the conductivity of the solution increases steadily without any inflection on the curve. With potassium fluorosulphonate, however, there is a definite minimum in the curve, the shape of which resembles the titration curve of antimonic fluoride with potassium fluorosulphonate. An electrolysis experiment, in which gold is deposited cathodically, appears to contradict the conclusion that auric fluoride is an acid, but it is not unusual for solutions of complex gold anions to deposit gold at cathodes (see Woolf, *J.*, 1954, 252). There is a possibility of amphoteric behaviour, since auric fluoride combines with sulphur trioxide. The compound isolated, $AuF_3,2{\cdot}7SO_3$, could be a mixture of fluorosulphonates but it is unsound to regard all compounds of fluorides with sulphur trioxide as fluorosulphonates.

In group III the extreme members boron and thallium trifluoride have been examined. The latter is insoluble, and the former about as soluble as in sulphuric acid or hydrocarbons (*ca.* 46 ml./g. at 15°). It is eliminated completely on being heated and presumably dissolves without reaction in the solvent. It seems that boron trifluoride is unable to displace sulphur trioxide from fluorosulphonic acid since even in the presence of potassium fluorosulphonate no tetrafluoroborate is formed. Stannic fluoride was too sparingly soluble (*ca.* 0·2 g./100 ml.) for any reliable conductometric titrations to be made.

In group V the most soluble trifluoride is that of arsenic. Antimony trifluoride is sparingly soluble, and bismuth trifluoride insoluble. Arsenic trifluoride gives a conductivity minimum with antimony pentafluoride but not with potassium fluorosulphonate, in contrast to tantalum pentafluoride which gives no inflection with antimony pentafluoride but transports tantalum to the anode on electrolysis. Antimony trifluoride also gives a minimum in the conductivity curve with the pentafluoride. Electrolysis of the solution shows a net transport of antimony to the cathode, although the electrolysis is complicated by oxidation of Sb^{III} to Sb^{V} and reduction to Sb^{0} at anode and cathode respectively. Thus the trifluorides of Group V behave as bases and the pentafluorides as acids in fluorosulphonic acid solutions. Interaction is possible between pairs of elements in different valency states.

The fluorides of group VI, which are under investigation by Robinson and his co-workers, have not been examined, but it appears likely that the quadrivalent fluorides will behave as bases. A compound SeF_4,SO_3 has already been formulated as SeF_3,SO_3F (Aynsley, Peacock, and Robinson, *J.*, 1952, 1231; Peacock, *J.*, 1953, 3617). The sexavalent fluorides, which form complexes with alkali fluorides under pressure (Martin, Albers, and Dust, *Z. anorg. Chem.*, 1951, **265**, 128), may react with tetrafluorides in fluorosulphonic acid solutions.

In group VII, bromine trifluoride and iodine pentafluoride react as bases since they can be titrated with antimonic fluoride but not potassium fluorosulphonate solutions. The bromine in bromine trifluoride solutions is transported in a cation. The behaviour of iodine pentafluoride as a base may explain a previous failure to prepare potassium hexafluoroiodate from potassium fluoride and iodine pentafluoride in hydrogen fluoride (*J.*, 1950, 3678). Iodine pentafluoride may form the base $IF_4^+HF_2^-$ rather than the acid $H^+IF_6^-$ in hydrogen fluoride solution. Rogers and Katz (*J. Amer. Chem. Soc.*, 1952, **74**, 1375) also postulate that bromine and iodine fluorides are basic in hydrogen fluoride. Rogers (personal communication) points out that the factor which may decide the mode of ionization is the large energy of ionization of hydrogen fluoride.

The only group VIII fluoride examined has been platinic fluoride which is sparingly soluble. An approximate titration shows that it is acidic with potassium fluorosulphonate.

In many of the titrations described, the end-points were nearer 2 : 1 or 3 : 1 proportions rather than 1 : 1. The simplest explanation in the case of bases is the formation of di- or tri-nuclear cations. For example, antimony pentafluoride was found equivalent to two molecules of the trifluoride so that the postulated reactions would be

$$2SbF_3 + HSO_3F \rightleftharpoons (Sb_2F_5)^+SO_3F^- + HF$$

and $$SbF_5 + HSO_3F \rightleftharpoons H^+SbF_6^- + SO_3$$

followed by $$(Sb_2F_5)^+SO_3F^- + H^+SbF_6^- \longrightarrow (Sb_2F_5)^+SbF_6^- + HSO_3F$$

Ruff and Plato's compound $SbF_5,2SbF_3$ (*loc. cit.*) may have this ionic structure, and the possibility of a polycation is strengthened by the existence of analogous polyanions in $CsSb_2F_7$ and $NaSb_4F_{13}$. The low molecular conductivity of antimony trifluoride, about a fifth of that of fluorosulphonates, shows that it is incompletely ionized as a fluorosulphonate. Another explanation may be that these fluorides react further with the solvent. That some reaction does occur is shown by a decrease in conductivity with time, of, *e.g.*, bromine trifluoride solutions. The formation of $S_2O_5F_2$ and $S_3O_8F_2$ which occurs under more drastic conditions with fluorides and sulphur trioxide (Hayek and Koller, *Monatsh.*, 1951, **82**, 940; Schmidt, *ibid.*, 1954, **85**, 452; Lehmann and Kolditz, *Z. anorg. Chem.*, 1953, **272**, 73) may occur to some extent with fluorides in fluorosulphonic acid. The di- and tri-sulphuryl fluorides would not be expected to ionize appreciably in fluorosulphonic acid, just as sulphuryl chloride is non-ionized in sulphuric acid. Further investigation will be required to elucidate these problems but our main thesis, that fluorides are separable into two divisions according to whether they titrate as acids or bases, is unaffected.

Perchloric acid solutions (see p. 442) resemble fluorosulphonates in that they can be titrated with antimony pentafluoride but not potassium fluorosulphonate. This leads to the unexpected conclusion that perchloric acid is a proton acceptor in fluorosulphonic acid. However, the presence of chlorine in a positive oxy-ion has been demonstrated recently by the preparation of the complex fluorides, $ClO_2^+BF_4^-$ and $ClO_2^+SbF_6^-$ (Schmeisser and Ebenhoech, *Angew. Chem.*, 1954, **66**, 230; Woolf, *J.*, 1954,) so that the existence of a septavalent chlorine oxy-cation is more acceptable. The ionization could be of the type $2HSO_3F + HClO_4 \rightleftharpoons ClO_3^- + H_3O^+ + 2SO_3F^-$. Examination of solutions of chloryl fluoride and nitryl fluoride in fluorosulphonic acid, which should react as bases, may throw some light on the nature of perchloric acid solutions.

Fluorosulphonic acid has been used to prepare simple fluorides and fluorosulphonates from oxides and halides (Engelbrecht and Grosse, *J. Amer. Chem. Soc.*, 1954, **76**, 2042;

Hayek, Puschmann, and Czaloun, *Monatsh.*, 1954, **85**, 359). The above work indicates that fluorosulphonic acid can also be applied to the preparation of complex fluorides by means of neutralization reactions. It would be premature, however, to attempt the latter without a clearer understanding of ionization in fluorosulphonic acid, and it is suggested that spectrometric and ebullioscopic techniques might be profitably employed with non-reactive solutes.

EXPERIMENTAL

Attempted Preparation of Group V Double Fluorides with Bromine Trifluoride.—The following pairs of fluorides were mixed (in practice the elements or oxides used were converted into fluorides by the solvent) : SbF_5–AsF_5, SbF_5–PF_5, AsF_5–VF_5, and SbF_5–TaF_5. The respective products were SbF_5,BrF_3, SbF_5,BrF_3, no residue, and mixture of SbF_5,BrF_3 and TaF_5,BrF_3. These mixtures cover all combinations of volatile and non-volatile acids. In all cases the products were those which would result if the fluorides reacted separately with the solvent.

Reactions in Arsenic Trifluoride (*J.*, 1950, 2200).—Antimony trifluoride (0·5 g.) was refluxed for an hour with arsenic trifluoride. The bulk of the solvent was removed by distillation at atmospheric pressure, the rest *in vacuo*, and the residue analysed (Found : F, 38·3; As, 24·4%; equiv., 314. SbF_3,AsF_3 requires F, 36·7; As, 24·1%; equiv., 311).

Antimony tri- and penta-fluoride were mixed in equimolar amounts in arsenic trifluoride and heated for a short time, and excess of solvent removed as above. The residue was found to be $SbF_3,0{\cdot}98SbF_5,0{\cdot}57AsF_3$ by analysis of tervalent elements iodometrically, total antimony as sulphide, and arsenic as sulphide. When the reactants were in the molar ratio $SbF_5 : SbF_3 =$ 411 : 1, the residue was $SbF_3,1{\cdot}09SbF_5,0{\cdot}09AsF_3$.

Conductivity of Fluorosulphonic Acid.—The acid was made by passing sulphur trioxide into excess of hydrogen fluoride. The excess was removed by warming in a stream of nitrogen, and the acid purified by two distillations at normal pressure in an apparatus with the minimum number of ground joints. The fraction of b. p. 163° ± 0·5° was collected, and a middle fraction (range 0·1°) was transferred to a tapless vacuum apparatus where it could be fractionated by trap-to-trap distillation, each trap being sealed in turn. The conductivity cell was connected to the last trap. (Platinum electrodes were joined to the Pyrex glass cell *via* graded seals. This type of seal only withstood one or two experiments before it broke under vacuum. Soft-glass seals held in ground joints were more durable but the most satisfactory arrangement was a platinum–Pyrex seal made vacuum-tight on the inside of the seal with a commercial melamine-formaldehyde resin cured at 200°.) Results were as follows :

Temp.	−78°	−74°	−20°	0°	25·0°	58·4°	25·0°
κ (mhos) $\times 10^4$	0·0727	0·112	0·82	1·38	2·24	5·52	2·52

The attack on glass was indicated by the increased conductivity value at 25° after the measurements above 50°. The activation energy of conduction obtained from the slope of the log κ–$1/T$ plot was 3·83 kcal. The activation energy of viscous flow is between 2·4 and 3·6 kcal. if Trouton's constant is assumed to be 22, and the activation energy of flow between one-third and one-quarter of the latent heat.

Electrolysis of Fluorosulphonic Acid.—The acid was distilled in *via H* (Fig. 1), which was then sealed. The apparatus was evacuated *via A*, the cell being cooled occasionally in liquid air so that the acid remained just molten. The platinum cylinder electrodes were spot-welded to platinum wires which were in turn silver-soldered to tungsten wire–Pyrex glass seals well above the electrolyte level. *E*–*F* and *C*–*B* were gas locks fitted as a precaution against any surge of gas. Once it had been established that gas evolution occurred at only one electrode, the apparatus from *C* to *A*, and tap *D*, were closed off. Electrolyses were initially made at 0° but appreciable amounts of acid vapour were carried over with the gas. This was much reduced by electrolysing at −78° at 20 mA and cooling trap *I* in liquid air for a time at the end of the run. The gas sample was removed in *J*, and its density found by direct weighing, the pressure and volume being known. It was analysed for oxygen in a modified Orsat apparatus, with negative results. The hydrogen content was found by heating it with copper at 300°. A typical analysis follows :

Initial gas pressure at 19·5°, 11·5 cm.; final, 1·7 cm. Weight of water residue 30·0 mg. (Weight of water expected if gas were 100% hydrogen is 29·2 mg. Vapour tension expected for water at 19·5° is 1·7 cm.). The density of the gas was about 3, the high value being due to traces of acid (*ca.* 2%). The volume of gas in the system, approximately estimated because of temperature differences in the apparatus, was 73·7 ml. at N.T.P. If one Faraday liberates half a molecule of hydrogen, then the 0·2206 g. of copper deposited in a series coulometer would be equivalent to 77·7 ml. Thus, on electrolysis, $H^+ + e^- \longrightarrow \frac{1}{2}H_2$. The percentage of acid electrolysed was 0·5%.

A complete electrolysis, *i.e.*, till gas evolution had ceased, was carried out with a current of 0·2 amp. on 1·5 ml. of acid at −78°, and the gas collected in a calibrated bulb and manometer. The gas evolution had practically ceased in 5 hr. :

Time (hr.)	0	1·0	3·6	5·0	5·85	6·5	9·0	10·15	11·7
Gas pressure (cm.)	0	1·00	2·90	3·45	3·55	3·65	3·55	3·70	3·75

One molecule of acid generated 5560 ml. of hydrogen at N.T.P., which corresponded to 0·25 mole of hydrogen (5600 ml.), *i.e.*, $2HSO_3F = \frac{1}{2}H_2 + HS_2O_6F_2$. The residue had the sweet odour of ozone or fluorine but its aqueous solution did not liberate iodine from iodides or oxidise ferrous or chromic salts. Presumably its oxidising properties were dissipated by liberation of oxygen from water.

Transport of Fluorine in the Acid.—Two simple devices (Fig. 2) were used to separate catholyte from anolyte at the end of electrolysis without the use of taps. In the first the connecting limb was inclined slightly out of the plane through the two compartments. The liquid could be divided by tilting the apparatus to produce a bubble at the constriction. A separation was effected in the second apparatus by pouring off liquid to just below the compartment level. In both apparatus some remixing does occur, especially on prolonged electrolysis, so the results are semi-quantitative. For solutions of hydrofluoric acid a cell of the second type in Polythene was used. The fluorine content was found by Willard and Winter's method after hydrolysis of equal volumes from cathode and anode compartments. The results are given in ml. of thorium nitrate solution :

FIG. 1.

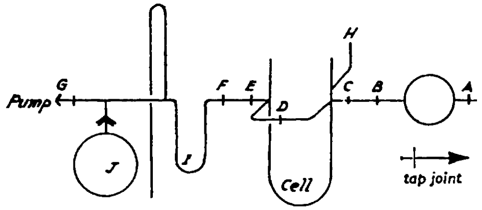
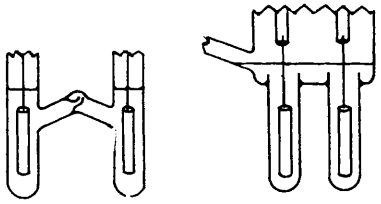


FIG. 2.



Electrolysis of the acid : anode samples, 261, 262; cathode samples, 248, 249. Electrolysis of hydrogen fluoride (2·60 g.) in fluorosulphonic acid (57·19 g.) : anode, 323, 326; cathode, 336, 332. Electrolysis of potassium fluoride (1·78 g.) in the acid (66·13 g.) : anode, 243; cathode, 239.

Conductivity of Solutions in Fluorosulphonic Acid.—Potassium fluorosulphonate. The salt was prepared in the dry way from " AnalaR " potassium persulphate and bromine trifluoride, the excess of solvent was removed *in vacuo*, and the powdered residue kept at 150° for 2½ hr. (Found : $KSO_3F/K_2S_2O_8$, 0·510. Calc. : 0·511). The salt, dissolved in water, was free from sulphate, bromide, persulphate, and fluoride. The acid was distilled into *A* at atmospheric pressure (Fig. 3), fractionated *in vacuo* to *B* and *C*, then poured into the cell, which was sealed and weighed. The solvent conductivity was checked, and the salt was then introduced in a stream of dry nitrogen by a weighing tube. The salt dissolved readily in the cold.

100 × Concn. (moles/kg. of solvent)	0	0·460	2·058	3·57	4·415
$10^3\kappa$ (at 25°)	0·495	1·594	5·46	9·00	10·94
(A) Molecular conductivity	—	239	240	241	237
(B) ,, ,, ...	—	346	266	255	248

(A) With solvent correction; (B) without.

The corresponding data for aqueous solution were given in Part I and those for solutions in bromine trifluoride were :

100 × Concn. (moles/kg. of solvent)	2·41	4·93	6·13	8·92
$10^3\kappa$ (at 25°)	11·25	13·10	14·01	15·50
(A) Molecular conductivity	135	116	98	84

(Solvent conductivity = 8·10 × 10^{-3} mho.)

Antimony trifluoride. The trifluoride was purified by Bak and Hillebert's method (*Acta Chem. Scand.*, 1953, 7, 236) and finally by sublimation. The solvent had to be heated to effect solution.

100 × Concn. (moles/kg. of solvent)	0·681	1·746	3·81	7·30
$10^4\kappa$ (at 25°)	4·99	8·50	13·90	20·62
(A) Molecular conductivity	39·9	36·0	30·7	25·2

Antimony pentafluoride. This was vacuum-distilled into small ampoules which were broken and dropped into the solvent.

100 × Concn. (moles/l.)	2·749	4·34	5·87	8·20
$10^4\kappa$ (at 25°)	30·44	41·75	50·4	61·8
(A) Molecular conductivity	97·6	87·9	79·8	71·0

The molecular conductivity extrapolated to infinite dilution by plotting against the square-root of concentration is 46·5 for the trifluoride and 136 for the pentafluoride.

Sulphur trioxide. Sulphur trioxide, prepared by heating 40% oleum, was purified by distillation from phosphorus pentoxide and finally by fractionation *in vacuo*. Specimens were sealed in ampoules which could be broken magnetically in a tapless apparatus, which included a purification line for the acid and a conductivity cell. The solvent showed a steady decrease in conductivity on addition of oxide. The solvent required warming to dissolve some of the trioxide which was in the asbestos-like form.

FIG. 3.

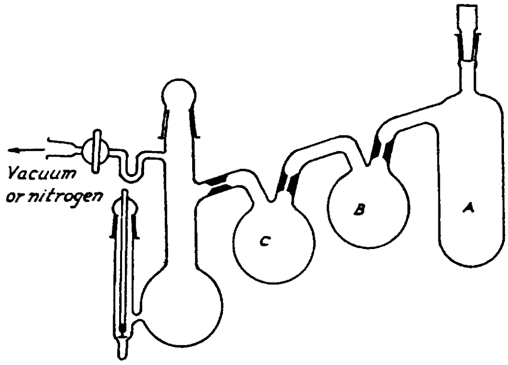
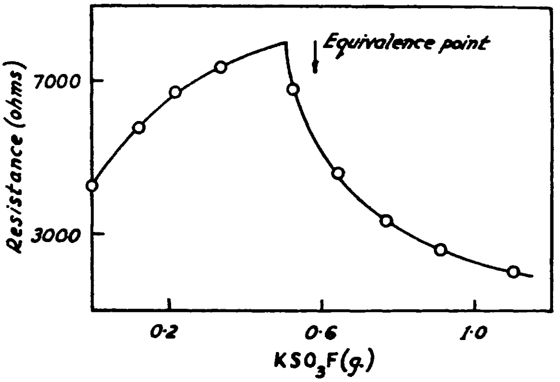


FIG. 4.



Molar ratio, SO_3/HSO_3F	0	0·273	0·550	0·807	0·943	1·243	1·402
$10^4\kappa$ (at 25°)	3·67	1·145	0·816	0·524	0·444	0·332	0·268

Conductometric Titrations.—The vacuum-distillation stage of purification was omitted in the purification of the acid, which consequently had a higher conductivity. Solutions were made by distillation of the solvent into a special type of weighing bottle, followed by addition of solids from weighing tubes, and of liquids either in ampoules or in weight pipettes. The conductivity cell was flushed with dry nitrogen and filled with the solution from one weighing bottle. The titrant was added in portions from another weighing bottle, and the conductivity measured between additions. The titrations are regarded as only approximate, because the solvent was not of the highest purity, the titrant volume was large (a correction has been made in some cases), the solutions and the solvent slowly attack even Pyrex glass, and some fluorides may react irreversibly with the solvent.

Antimony pentafluoride with potassium fluorosulphonate. SbF_5 (0·92 g.) in HSO_3F (89·9 g.). KSO_3F (1·11 g.) in HSO_3F (44·4 g.). The curve is shown in Fig. 4. The initial conductivity was $4·08 \times 10^{-3}$.

Pyridine with antimony pentafluoride. Pyridine (0·89 g.) in HSO_3F (94·6 g.). SbF_5 (4·09 g.) in HSO_3F (84·6 g.). The curve (Fig. 5) was corrected for dilution by multiplying the observed resistances by the factor $V/(V + v)$, where V was the volume of pyridine solution, and v that of titrant.

Nitrobenzene with antimony pentafluoride. $C_6H_5{\cdot}NO_2$ (0·64 g.) in HSO_3F (106·8 g.). SbF_5 (2·44 g.) in HSO_3F (35·2 g.). This curve (Fig. 5) was also corrected.

Auric fluoride with potassium fluorosulphonate. AuF_3 (0·86 g.) in HSO_3F (85·3 g.). KSO_3F (1·31 g.) in HSO_3F (394 g.).

Resistance (ohms) ...	2447	3954	5688	5184	3496	2607	2040	1657	1225
KSO_3F (g.)	0	0·094	0·183	0·361	0·468	0·592	0·742	0·904	1·300

End-point: 0·275 g. of KSO_3F; hence $KSO_3F \approx 2AuF_3$.

Antimony pentafluoride with auric fluoride. SbF_5 (0·587 g.) in HSO_3F (82·3 g.). AuF_3 (1·23 g.) in HSO_3F (84·6 g.).

Resistance (ohms)	6135	4884	3924	3336	3035	2817	2670	2533	2412	2308	2235
AuF_3 (g.)	0	0·113	0·204	0·317	0·410	0·512	0·605	0·720	0·866	1·039	1·229

Arsenic trifluoride with antimony pentafluoride. AsF_3 (0·44 g.) in HSO_3F (92·0 g.). SbF_5 (1·656 g.) in HSO_3F (60·1 g.).

Resistance (ohms)	16,060	18,580	14,098	10,220	6830	6073
SbF_5 (g.)	0	0·221	0·303	0·448	0·785	0·960

End-point at 0·26 g. SbF_5; hence, $SbF_5 \approx 3AsF_3$.

FIG. 5.

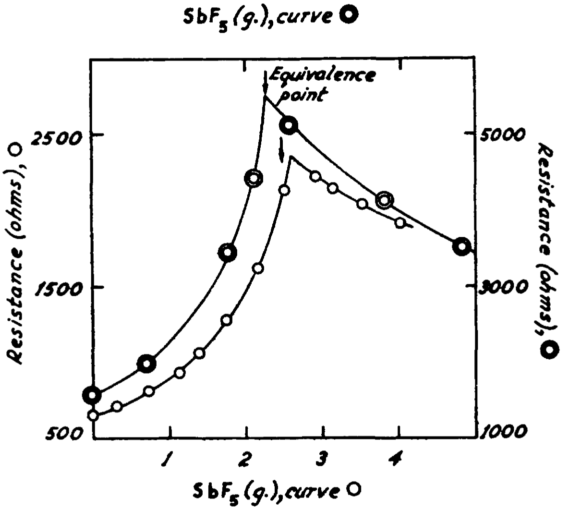
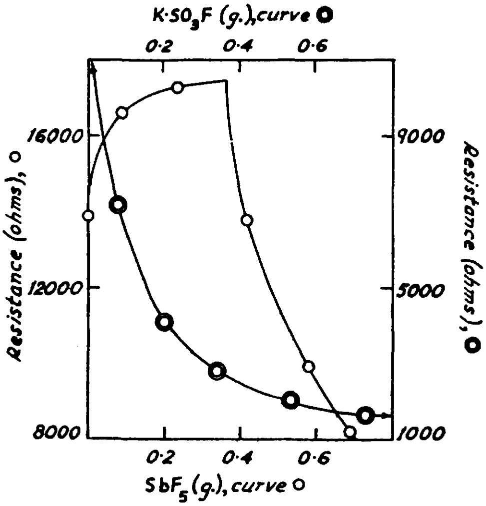


FIG. 6.



Arsenic trifluoride with potassium fluorosulphonate. AsF_3 (0·53 g.) in HSO_3F (97·0 g.). KSO_3F (0·93 g.) in HSO_3F (25·9 g.).

Resistance (ohms)	16,760	5031	2910	1911	1473	1330
KSO_3F (g.)	0	0·156	0·289	0·522	0·794	0·92

Antimony trifluoride with antimony pentafluoride. SbF_3 (0·30 g.) in HSO_3F (109·0 g.). SbF_5 (1·97 g.) in HSO_3F (110·5 g.).

Resistance (ohms) ...	18,500	24,390	25,360	23,170	19,310	16,020	14,030	12,555	11,310
SbF_5 (g.)	0	0·083	0·136	0·21	0·32	0·43	0·51	0·62	0·72

End-point at 0·19 g. SbF_5; hence $SbF_5 \approx 2SbF_3$.

Antimony pentafluoride with tantalum pentafluoride. SbF_5 (0·63 g.) in HSO_3F (89·9 g.). TaF_5 (1·55 g.) in HSO_3F (70·2 g.).

Resistance (ohms) ...	6773	7275	7604	8255	8643	9143	9707	10,430	10,998
TaF_5 (g.)	0	0·116	0·200	0·402	0·538	0·706	0·928	1·244	1·541

Bromine trifluoride with potassium fluorosulphonate and antimony pentafluoride. BrF_3 (0·60 g.) in HSO_3F (88·4 g.). KSO_3F (0·98 g.) in HSO_3F (40·8 g.). BrF_3 (0·46 g.) in HSO_3F (93·4 g.). SbF_5 (1·66 g.) in HSO_3F (60·1 g.).

Both titration curves are shown in Fig. 6.

The end-point is at 0·38 g. SbF_5; hence $SbF_5 \approx 2BrF_3$.

Iodine pentafluoride with potassium fluorosulphonate. IF_5 (0·75 g.) in HSO_3F (98·1 g.). KSO_3F (0·73 g.) in HSO_3F (52·0 g.).

Resistance (ohms)	6175	4228	3334	2944	2166	1892	1627
KSO_3F (g.)	0	0·084	0·160	0·249	0·396	0·54	0·71

Iodine pentafluoride with antimony pentafluoride. IF_5 (0·71 g.) in HSO_3F (88·1 g.). SbF_5 (1·65 g.) in HSO_3F (43·0 g.).

Resistance (ohms)	15,190	24,370	13,680	9700	7241	6396	5480
SbF_5 (g.)	0	0·15	0·41	0·64	1·00	1·22	1·62

End-point at 0·24 g. SbF_5; hence $SbF_5 \approx 3IF_5$.

Platinum tetrafluoride with potassium fluorosulphonate. Because of the low solubility of the tetrafluoride, all that could be shown was a rise in resistance on addition of a small amount of fluorosulphonate solution followed by a decrease on further addition.

Perchloric acid with potassium fluorosulphonate. $HClO_4$ (0·477 g.) in HSO_3F (106·8 g.). KSO_3F (1·04 g.) in HSO_3F (51·1 g.).

Resistance (ohms)	12,390	6894	4024	2522	1937	1685	1470
KSO_3F (g.)	0	0·098	0·235	0·45	0·66	0·81	1·03

Perchloric acid with antimony pentafluoride. $HClO_4$ (0·55 g.) in HSO_3F (56·0 g.). SbF_5 (1·68 g.) in HSO_3F (35·6 g.).

Resistance (ohms)	6670	7290	4922	4310	3940	3827
SbF_5 (g.)	0	0·44	0·89	1·18	1·52	1·66

End-point at 0·58 g. SbF_5; hence $SbF_5 \approx 2HClO_4$.

Electrolyses of Fluoride Solutions.—Silver fluoride. The fluoride (0·69 g.) was electrolysed in fluorosulphonic acid (39·9 g.) at approximately 20 mA. Silver (0·313 g.) was deposited at the cathode, the liquid in the anode compartment became black, and a black solid was deposited on the anode. The initial concentration (14·8 mg. of silver/g. of solution) increased to 20·4 at the cathode and was reduced to 9·2 at the anode. The black anode deposit, presumably of bivalent silver, contained only 40·4% of silver (Calc. for AgF_2: Ag, 74·0. Calc. for $AgSO_3F$: Ag, 52·2%).

Auric fluoride. Gold (0·706 g.) was converted into the trifluoride and dissolved in the acid (41·1 g.) to give an initial concentration of 17·2 mg./g. of solution. The final cathode concentration was 19·1 and the anode concentration 13·8 mg./g. A black deposit of gold covered the cathode. This was dissolved in cold aqua regia and separated from platinum by reduction by quinol after removal of nitric acid. No gas was evolved at the cathode.

Antimony pentafluoride. The pentafluoride (1·26 g.) in fluorosulphonic acid (44·0 g.) was electrolysed at approximately 20 mA until 0·00295 Faraday had passed. Samples were analysed iodometrically for tervalent and total antimony. The latter was precipitated as sulphides and reduced by boiling with concentrated hydrochloric acid. The initial antimony concentration found by analysis was 15·64 mg./g. of solution (Calc.: 15·74 mg./g.). The final concentrations were 17·64 and 13·13 mg./g. at anode and cathode respectively. The antimony balance showed that part had been reduced to Sb^0 and Sb^{III} at the cathode. The deposit on the latter was dissolved in concentrated sulphuric acid for analysis. The results, in mg. of antimony, were:

Anode compartment: Initial, 313. Final, 353.
Cathode ,, ,, 317. ,, 277.

The final anode quantity includes 11·5 mg. of Sb^{III}, and the cathode 26 mg. of Sb^{III} and 11 mg. of Sb^0 (electrode deposit).

Antimony trifluoride. A solution (36·4 g.) which contained 10·39 mg. of Sb^{III}/g. was electrolysed at about 12 mA (0·00247 Faraday passed):

Cathode compartment: Initial, 200. Final, 209.
Anode ,, ,, 175. ,, 165.

The final anode quantity included 132 mg. of Sb^V, and the cathode 52 mg. of Sb^0 (electrode deposit).

Tantalum pentafluoride. The initial tantalum concentration (15·9 mg./ml.) increased to 17·0 at the anode, and decreased to 14·5 at the cathode. The tantalum precipitated as hydroxide with ammonia was ignited and then extracted repeatedly with hydrofluoric acid to remove silica.

Bromine trifluoride. The trifluoride (1·66 g.) in the acid (54·3 g.) produced no hydrogen on electrolysis. In the catholyte a brown lower layer appeared which moved slowly upwards. Analysis by precipitation of silver bromide showed that the cathode contained more bromine than the anode.

Most of this work was carried out during 1953 when the author was a Turner and Newall Fellow. He is indebted to the Imperial Smelting Corporation for the generous gifts of fluorosulphonic acid used in conductometric titrations.

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