tures in relatively high yields[11] with the occurrence of only small quantities of B_2H_6. Although there is evidence that reaction 1 may proceed by a more devious course under different circumstances,[12] the relatively

(11) L. Lynds and D. R. Stern, British Patents 853,379 (Nov. 9, 1960); 852,312 (Oct. 26, 1960).

(12) H. W. Myers and R. F. Putnam, *Inorg. Chem.*, **2**, 655 (1963).

slow rate of disproportionation at room temperature presents an interesting candidate for a kinetic study which could be followed spectrophotometrically.

Acknowledgment.—The authors are indebted to Dr. Milton Blander for helpful discussions concerning thermodynamic topics in this paper.

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The Fluorosulfuric Acid Solvent System.
# I. Electrical Conductivities, Transport Numbers, and Densities[1]

BY J. BARR, R. J. GILLESPIE, AND R. C. THOMPSON

The results of measurements of the conductivities and transport numbers of solutions of some alkali and alkaline earth metal fluorosulfates in fluorosulfuric acid are reported. It is concluded that the fluorosulfate ion conducts mainly by a proton-transfer process. Conductometric studies of a number of other bases are reported. Dissociation constants are calculated for several weak bases. Densities of solutions of a number of solutes have been measured.

Introduction

Fluorosulfuric acid ionizes as a weak acid in dilute solution in the very weakly basic solvent sulfuric acid.[2a]

$$HSO_3F + H_2SO_4 = H_3SO_4{}^+ + SO_3F^-$$
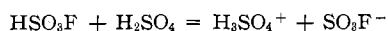
This behavior suggests that pure liquid fluorosulfuric acid might be a still more acidic and less basic medium than 100% sulfuric acid.

Since there has only been one previous study of fluorosulfuric acid as a solvent system,[2b] a study has been conducted in this laboratory which has given the results reported in this and subsequent papers of this series.

A comparison of some of the physical properties of fluorosulfuric acid with those of sulfuric acid shows that, in addition to its greater acidity, fluorosulfuric acid has a lower boiling point (162.7° *vs.* 290–317° for H_2SO_4), a lower viscosity than sulfuric acid (1.56 *vs.* 24.54 cp. at 25°), and a very low freezing point (−89.0° *vs.* 10.37° for H_2SO_4). The density is 1.7264 g./cc. at 25° compared with 1.8267 g./cc. for H_2SO_4.

Experimental

Purification and Conductivity of Fluorosulfuric Acid.—Commerical fluorosulfuric acid (Allied Chemical Co.) was purified by double distillation at atmospheric pressure in a completely enclosed all-glass apparatus, which had been carefully dried by flaming under a stream of dry air. In the second distillation a constant-boiling fraction was collected directly in the conductivity cell. This acid generally had a conductivity in the range 1.09 to 1.4×10^{-4} ohm^{-1} cm.$^{-1}$. The conductivity of any given sample did not increase by more than 0.5% during twelve or more hours standing. It was not possible to reduce the conductivity of the acid by further distillation to less than 1.085×10^{-4} ohm^{-1} cm.$^{-1}$. This is the lowest conductivity that we have observed for the

(2) (a) J. Barr, R. J. Gillespie, and E. A. Robinson, *Can. J. Chem.*, **39**, 1266 (1961); (b) A. A. Woolf, *J. Chem. Soc.*, 433 (1955).

acid. The twice-distilled acid had a boiling point of 162.7 ± 0.1°, in excellent agreement with the value reported originally by Thorpe and Kirman.[3] The small variations in the conductivity of different samples of the acid may be attributed to the presence of very small and variable amounts of impurities, such as water. As there is probably a very slight decomposition of the acid into HF and SO_3 even at room temperature which may become appreciable at the boiling point of the acid, and as there may be some fractionation in the distillation, there may be small variable amounts of free SO_3 or HF in the distilled acid. Woolf[2b] also found a variation in the conductivity of different samples of the acid, but the lowest conductivity that he reported was 2.2×10^{-4} ohm^{-1} cm.$^{-1}$. He purified the acid by trap to trap distillation under reduced pressure. This could have given a distillate which contained more free HF than that present in the acid purified by distillation at atmospheric pressure. Hydrogen fluoride is a weak base in the fluorosulfuric acid solvent system and this could account for the high conductivity of the acid prepared by Woolf.

Conductivity Measurements.—The design of the cell used in measuring the conductivities of solutions in fluorosulfuric acid was similar to that used previously for sulfuric acid solutions[4] except that it contained three electrodes and had cell constants of approximately 2 and 40. Thus, a wide range of electrolyte concentrations could be covered by successive additions of electrolyte to the solution in the cell. The capacity of the cell was approximately 200 ml. The electrodes were plated with platinum black.[5]

In the early stages of this work the cells were calibrated using aqueous potassium chloride solution.[6a] Although this method is very accurate it was later found more convenient to calibrate the cells by measuring the resistance of minimum-conducting sulfuric acid.[6b] All measurements were made in an oil thermostat at 25 ± 0.002°.

Solid solutes were added to the cell by means of a weight buret with a wide-bore tap. After each addition of solute the cell was shaken well to ensure good mixing and placed in the thermostat.

(3) T. E. Thorpe and W. Kirman, *ibid.*, 921 (1892).

(4) R. J. Gillespie, J. V. Oubridge, and C. Solomons, *ibid.*, 1804 (1957).

(5) G. Jones and D. M. Bollinger, *J. Am. Chem. Soc.*, **57**, 280 (1935).

(6) (a) J. E. Lind, J. J. Zwolinek, and R. M. Fuoss, *ibid.*, **81**, 1557 (1959); (b) R. J. Gillespie, J. V. Oubridge, and C. Solomons, *J. Chem. Soc.*, 1804 (1957).

The resistance was measured after temperature equilibrium had been reached in 10 to 15 min. The cell was then removed from the thermostat, again shaken, and the resistance measurement repeated. In this manner errors due to inadequate mixing were eliminated. Resistances of solutions were measured using a Leeds and Northrup, Jones conductivity bridge.

Transport Number Measurements.—The transport number of the barium ion was determined by the Hittorf method using a transport number cell, similar in design to the one used by Gillespie and Wasif.[7] The experimental procedure was essentially the same as that described by these authors. A current of 20 ma. was passed through the solution for 2–3 hr. from a Sargent coulometric current source. After electrolysis the cell compartments were separated and, from the level of liquid in graduated capillary side arms attached to the cathode and anode compartments, the total volume of solution in each was determined. Aliquot samples were taken from each compartment, the excess fluorosulfuric acid was removed, and the barium content of the residue was determined as barium sulfate.

The cell used for determining the transport number of the potassium ion had compartments that could be separated from each other at ground-glass joints located in the connecting arms. The quantity of solution in each compartment was determined by weighing each compartment separately. Potassium was then determined as potassium sulfate. Weighed portions from each compartment were evaporated to dryness in a platinum crucible and the residue of potassium fluorosulfate was converted to sulfate by evaporation to constant weight with sulfuric acid.

Viscosity of Fluorosulfuric Acid.—The viscosity of fluorosulfuric acid was found to be 1.56 cp. at 25° using an Ostwald viscometer which was calibrated with five glycerol solutions whose viscosities were found by measuring their specific gravities and using a combination of the data of Sheely[8] and the Chemical Rubber Publishing Co.[9]

Densities.—These measurements were made with a 10-ml. specific gravity bottle. The results are given in Table I. In those cases where measurements were made at several concentra-

TABLE I

DENSITIES OF FLUOROSULFURIC ACID SOLUTIONS AT 25°

$10^2 m$	d^{25}_4	$10^2 m$	d^{25}_4
KSO₃F		**Ca(SO₃F)₂**	
0	1.7264	15.33	1.7547
2.271	1.7283	34.86	1.7945
5.746	1.7317		
8.967	1.7348	**Ba(SO₃F)₂**	
11.92	1.7379	2.361	1.7346
18.85	1.7439	3.039	1.7371
NH₄SO₃F		7.353	1.7533
1.854	1.7270	10.97	1.7659
3.950	1.7278	12.99	1.7707
9.853	1.7300		
13.91	1.7313	Acetic acid	
RbSO₃F		3.116	1.7267
3.458	1.7315	7.011	1.7264
5.590	1.7347	11.37	1.7265
11.72	1.7438		
15.12	1.7479	Nitro compounds	
NaSO₃F		15.44	1.7158[a]
4.837	1.7303	11.53	1.7214[b]
13.61	1.7341	15.54	1.7177[c]
LiSO₃F		10.93	1.7230[d]
108.3	1.7826	12.35	1.7251[e]
119.0	1.7889		

[a] C₆H₅NO₂.   [b] p-NO₂C₆H₄Cl.   [c] 2,4-(NO₂)₂C₆H₃CH₃.   [d] m-NO₂C₆H₄Cl.   [e] 2,4-(NO₂)₂C₆H₃Cl.

(7) R. J. Gillespie and S. Wasif, *J. Chem. Soc.*, 209 (1953).
(8) M. L. Sheely, *Ind. Eng. Chem.*, **24**, 1060 (1932).
(9) "Handbook of Chemistry and Physics," 34th Ed., Chemical Rubber Publishing Co., Cleveland, Ohio, 1952, p. 1895.

tions the density was found to be a linear function of the molality.

Preparation and Analysis of Fluorosulfates.—Alkali and alkaline earth fluorosulfates were prepared by the reaction of the anhydrous chloride with fluorosulfuric acid. Fluorosulfuric acid was distilled onto the anhydrous salt in an atmosphere of dry air at 25° and HCl and excess solvent were removed by heating to 100° under vacuum for approximately 2 days. The product was handled in a drybox and stored in sealed glass ampoules. Ammonium fluorosulfate was crystallized from an ice-cold aqueous solution adjusted to pH 7 and containing equivalent amounts of ammonium hydroxide and fluorosulfuric acid. NH₄SO₃F, KSO₃F, and RbSO₃F were recrystallized from water, washed twice with small quantities of water, then with acetone and ether, and stored over phosphoric oxide in a vacuum desiccator.

For analysis a sample was dissolved in water and 10-ml. aliquots were heated at 121° in a stream of dry air for several hours in order to hydrolyze the fluorosulfate and to remove the HF formed. The residue was redissolved in water and sulfate was determined as barium sulfate. In the case of barium and strontium fluorosulfates barium and strontium were determined rather than sulfate. The fluorine in the distillate obtained from heating a sample with 60% perchloric acid was determined as PbClF.

Anal. Calcd. for KSO₃F: F, 13.7; S, 23.2. Found: F, 13.1; S, 22.6. Calcd. for NaSO₃F: F, 15.6; S, 26.3. Found: F, 15.4; S, 26.0. Calcd. for LiSO₃F: F, 17.9; S, 30.2. Found: F, 17.7; S, 30.2. Calcd. for Sr(SO₃F)₂: F, 13.3; Sr, 30.7. Found: F, 13.1; Sr, 30.4. Calcd. for Ba(SO₃F)₂: F, 11.3; Ba, 40.9. Found: F, 11.2; Ba, 40.4.

In all cases freshly made solutions of the fluorosulfates gave negative tests for chloride and sulfate.

Acetic Acid.—Analar grade acetic acid was purified by fractional freezing and used immediately.

Benzoic Acid.—Analar grade benzoic acid was recrystallized from water and dried over phosphoric oxide in a vacuum desiccator.

Nitro Compounds.—Nitrobenzene and m-nitrotoluene were purified by fractional freezing followed by distillation. 2,4-Dinitrotoluene, m-nitrochlorobenzene, p-nitrochlorobenzene, and 2,4-dinitrochlorobenzene were recrystallized twice from methanol and stored over phosphoric oxide in a vacuum desiccator. Trinitrobenzene was prepared by decarboxylation of trinitrobenzoic acid and was recrystallized from glacial acetic acid, washed with water, then dried and stored over phosphoric oxide in a vacuum desiccator (m.p. 119–121°).

Antimony Trifluoride.—The commercial material was recrystallized from dry methanol and sublimed in a Monel apparatus in an atmosphere of dry nitrogen.

Arsenic Trifluoride.—This substance was prepared by the reaction of arsenic trioxide with calcium fluoride and concentrated sulfuric acid (b.p. 57°).

Sulfuric Acid.—Sulfuric acid (100%) was prepared as described previously.[6]

Results and Discussion

Solutions of Metal Fluorosulfates.—By analogy with other protonic solvent systems, we assume that fluorosulfuric acid undergoes autoprotolysis

$$2HSO_3F \rightleftharpoons H_2SO_3F^+ + SO_3F^-$$

Bases in this system may then be defined as substances which, when dissolved in fluorosulfuric acid, increase the concentration of the fluorosulfate ion SO₃F⁻, while an acid may be defined as any substance which increases the concentration of the fluorosulfuric acidium ion H₂SO₃F⁺. The alkali and alkaline earth metal fluorosulfates are therefore expected to behave as strong bases in this system. The results of our conductivity measurements on solutions of metal fluorosulfates in fluorosulfuric acid at 25° are given in Table II.

TABLE II

SPECIFIC CONDUCTANCES OF SOME ALKALI AND ALKALINE EARTH METAL FLUOROSULFATES AT 25°

$10^2 m$	$10^2 c$	$10^4 \kappa$, ohm^{-1} cm.$^{-1}$
	LiSO₃F	
0.80	1.38	21.29
1.61	2.78	41.36
2.74	4.72	67.98
3.09	5.33	75.10
4.13	7.11	97.00
5.63	9.69	129.1
6.63	11.39	151.2
7.21	12.38	161.6
8.34	14.31	185.4
8.87	15.21	194.3
9.96	17.24	215.2
10.19	17.48	220.8
11.81	20.22	248.9
12.10	20.70	249.3
14.20	24.28	291.8
	NaSO₃F	
0.48	0.82	12.98
1.30	2.25	32.61
1.70	2.93	42.69
3.34	5.76	80.15
4.05	6.95	95.54
5.56	9.55	128.2
5.74	9.87	132.2
8.19	14.06	181.3
9.43	16.14	205.5
10.89	18.64	233.2
13.17	22.48	274.1
13.58	23.19	280.8
16.09	27.43	322.7
	NH₄SO₃F	
0.000	0.000	1.085
0.047	0.081	1.841
0.138	0.238	4.171
0.191	0.330	5.504
0.199	0.344	5.892
0.289	0.499	8.189
0.346	0.597	9.561
0.423	0.730	11.710
0.468	0.808	12.907
0.703	1.213	19.03
1.001	1.726	26.74
1.217	2.098	32.25
1.282	2.210	33.86
1.770	3.050	46.00
3.24	5.579	81.09
4.40	7.56	108.02
5.43	9.32	131.08
6.05	10.39	144.85
7.09	12.16	167.19
7.78	13.33	181.89
9.07	15.52	208.5

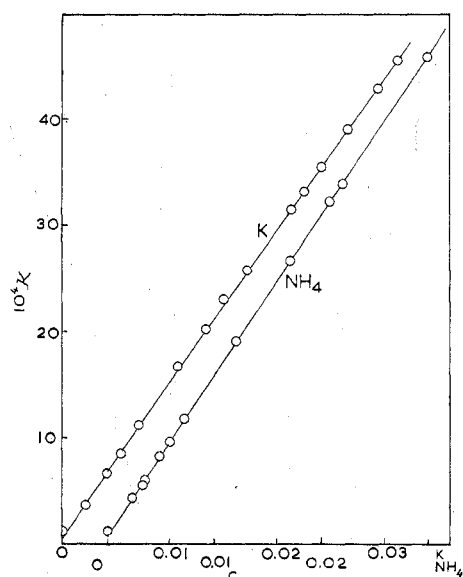| $10^2 m$	$10^2 c$	$10^4 \kappa$, ohm^{-1} cm.$^{-1}$
	KSO₃F	
0.000	0.000	1.085
0.115	0.199	3.586
0.238	0.411	6.679
0.315	0.544	8.443
0.411	0.709	11.191
0.624	1.076	16.758
0.778	0.342	20.23
0.869	1.500	23.09
1.000	1.725	25.84
1.240	2.139	31.63
1.243	2.144	31.56
1.308	2.256	33.26
1.398	2.411	35.52
1.544	2.662	39.10
1.706	2.941	43.00
1.813	3.125	45.67
2.03	3.50	50.73
3.65	6.28	88.50
4.94	8.49	117.28
5.82	9.99	136.17
6.39	10.97	148.24
7.16	12.29	164.28
8.39	14.39	189.10
10.14	17.36	223.04
12.41	21.20	264.80
14.43	24.62	299.92
	RbSO₃F	
0.55	0.94	14.24
0.73	1.26	18.82
0.97	1.67	24.74
2.30	3.96	56.16
3.07	5.28	74.76
3.46	5.95	83.49
8.00	13.70	180.1
11.04	18.86	240.0
12.32	21.02	263.9
15.12	25.73	313.4
	Sr(SO₃F)₂	
0.337	0.584	16.03
0.921	1.589	39.47
1.69	2.92	67.22
2.76	4.75	102.6
3.92	6.76	138.0
4.84	8.33	164.2
6.12	10.52	197.6
7.02	12.05	220.1
8.41	14.42	252.6
10.08	17.27	288.8
	Ba(SO₃F)₂	
0.120	0.210	6.83
0.439	0.760	21.32
0.653	1.12	29.01
1.16	2.01	50.30
1.43	2.46	62.22
1.61	2.78	66.55
2.11	3.68	87.88
2.85	4.91	110.32
3.76	6.47	140.32
4.93	8.47	176.27
6.05	10.36	212.90
7.35	13.01	244.54

Fig. 1.—Specific conductances of solutions of KSO₃F and NH₄SO₃F at low concentrations.

molar units by making use of the densities in Table I. In each case a plot of κ against molarity was found to be linear at low concentrations (Fig. 1). On extrapolation of the linear portions to zero concentration the curves do not pass through the origin nor through the initial point corresponding to the solvent conductivity. There must therefore be some curvature of the conductivity curve at the very lowest concentrations although this was not directly observed. The conductivity of the solvent may be attributed at least partly to its autoprotolysis. If the conductivity of the pure solvent is due only to the autoprotolytic ions the linear portion of the conductivity curve should pass through the origin on extrapolation. However, extrapolation gives a conductivity at zero concentration of approximately 5×10^{-5} ohm^{-1} cm.$^{-1}$. This can be attributed to ions other than the autoprotolytic ions while the remainder of the conductivity of the solvent, *i.e.*, 6×10^{-5} ohm^{-1} cm.$^{-1}$, can be attributed to the autoprotolytic ions. These other ions presumably arise from an excess of either SO₃ or HF or some other impurity or from SO₃ and HF present together as a result of self-dissociation of the solvent

$$HSO_3F \rightleftharpoons SO_3 + HF$$
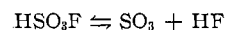
Ions would then arise from the ionization of HF, which behaves as a weak base

$$HF + HSO_3F = H_2F^+ + SO_3F^-$$
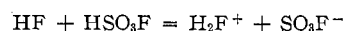
and from the ionization of SO₃, which behaves as a very weak acid.

$$SO_3 + 2HSO_3F = H_2SO_3F^+ + S_2O_6F^-$$
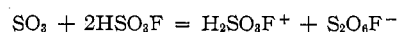
Added fluorosulfate ion will repress the basic dissociation of HF and enhance the acid dissociation of SO₃. In the absence of quantitative information on these equilibria it is not possible to predict exactly how they will be affected but by analogy with the effect of bases on the analogous self-dissociation equilibria of sulfuric

Since all the solutions were made up by weight the concentrations are expressed in molal units and also in

<div align="center">Table III

Interpolated Specific Conductances Corrected for the Solvent Conductivity</div>

10^2c	NH$_4$SO$_3$F	RbSO$_3$F	KSO$_3$F	NaSO$_3$F	LiSO$_3$F	Ba(SO$_3$F)$_2$	Sr(SO$_3$F)$_2$
1.0	15.3	14.8	14.8	14.8	14.8	27.0	25.7
2.0	30.3	29.4	29.4	28.7	28.7	50.2	48.2
3.0	44.6	43.6	43.6	42.9	42.9	72.7	69.0
4.0	58.6	37.3	57.3	56.8	56.8	94.0	88.2
5.0	72.5	71.0	71.0	70.4	70.4	114.5	106.6
6.0	86.4	84.4	84.4	83.4	83.4	134.0	124.6
8.0	113.3	110.4	110.4	108.3	108.2	168.7	158.5
10.0	139.3	136.0	135.7	132.7	132.6	200.5	190.0
12.0	164.5	160.7	160.3	156.4	156.6	230.3	219.5
14.0	189.3	184.8	184.2	179.2	180.0		247.0
16.0	213.8	207.8	207.0	202.4	203.2		273.0
20.0		252.2	251.1	247.0	247.2		
24.0		294.7	293.0	287.4	287.7		

$10^4\kappa$, ohm^{-1} cm.$^{-1}$

acid[10] it may be predicted that the total concentration of H$_2$F$^+$ and S$_2$O$_6$F$^-$ will remain approximately constant and thus these two ions will make a contribution to the conductivity that is approximately independent of the concentration of the added fluorosulfate. We therefore regard that part of the conductivity of the solvent that is not due to the autoprotolytic ions but is due to the ions H$_2$F$^+$ and S$_2$O$_6$F$^-$ or to the ions formed by some impurity as being at least approximately constant and independent of the concentration of added bases. Thus for any solution we have corrected the observed conductivity by means of the expression

$$\kappa_{cor} = \kappa_{obsd} - (\kappa_{solv} - \kappa_{ap})$$

where $\kappa_{ap} = 6 \times 10^{-5}$ ohm^{-1} cm.$^{-1}$. Interpolated values of these corrected conductivities at round molar concentrations are given in Table III. Some error is involved in the use of this expression if any impurity present (*e.g.*, water) represses the autoprotolysis. However, in the case of the accurate data obtained for potassium and ammonium fluorosulfates the solvent had a very low conductivity and the amount of any impurity other than HF or SO$_3$ must have been very small.

The conductivities of the alkali metal fluorosulfates are all very similar and at any given concentration they decrease slightly in the order NH$_4$ > Rb ~ K > Na ~ Li. The conductivities of Ba(SO$_3$F)$_2$ and Sr(SO$_3$F)$_2$ are also quite similar, although the conductivity of the strontium salt is slightly less than that of the barium salt. The small differences in the conductivities of the metal fluorosulfates may be attributed to an increase in the extent of solvation of the cations in the series NH$_4$ < Rb ~ K < Na ~ Li < Ba < Sr. This agrees reasonably well with the order that would be expected on the basis of size and charge of the cations and is also generally consistent with the degrees of solvation of these cations in sulfuric acid.[11]

Transport Numbers.–The similarities in the conductivities of the univalent fluorosulfates and of the divalent fluorosulfates clearly indicate that the major part of the current is carried by the common ion, *i.e.*,

by the fluorosulfate ion. This conclusion is confirmed by the very small values of 0.11 ± 0.03 and 0.075 ± 0.02 obtained for the cation transport numbers for solutions of potassium and barium fluorosulfates, respectively. The large probable errors in the transport numbers are due to limitations in the accuracy of the analytical methods used. Since the cation transport numbers are so small, extremely accurate analysis is required to detect the very small transport of the cation. The accuracy of the results was not sufficient to detect any variation in the transport numbers with concentration.

The abnormal mobility of the fluorosulfate ion is presumably a consequence of a proton-transfer mechanism of conduction. The autoprotolysis ions of water and sulfuric acid are known to conduct by such a mechanism.[11,12] It will be shown in a later paper that the fluorosulfuric acidium ion, H$_2$SO$_3$F$^+$, also conducts by a proton-transfer mechanism.

Equivalent Conductivities.–A plot of the equivalent conductivities for KSO$_3$F and NH$_4$SO$_3$F at low concentrations against the square root of the ionic strength $I^{1/2}$ is shown in Fig. 2. The equivalent conductivity appears to decrease approximately linearly with concentration up to $I^{1/2} = 0.18$, and at higher concentrations it decreases rather more rapidly than would be expected from this linear relation. Similar behavior has been observed for relatively concentrated aqueous hydrochloric acid soutions[13] and for solutions in sulfuric acid.[11] The reorientation of solvent molecules that are in solvation shells of ions is presumably more difficult than for "free" solvent molecules and hence such solvent molecules will contribute less effectively to the proton-transfer conduction process, since this must involve a reorientation step which may even be the rate-determining step for the whole process.[10,13] Thus as the concentration of the electrolyte is increased the number of solvent molecules that are "tied-up" in solvation shells increases and the proton-transfer conduction process is correspondingly hindered.[14]

Extrapolation of the Λ–$I^{1/2}$ curves to zero ionic

(10) S. J. Bass, R. J. Gillespie, and E. A. Robinson, *J. Chem. Soc.*, 820 (1960).
(11) R. H. Flowers, R. J. Gillespie, E. A. Robinson, and C. Solomons, *ibid.*, 4327 (1960).
(12) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Academic Press, Inc., New York, N. Y., 2nd Ed., 1959, p. 121.
(13) Reference 12, p. 372.
(14) L. Onsager, *Ann. N. Y. Acad. Sci.*, **46**, 265 (1945).

strength gave the following values for Λ_0, the equivalent conductance at infinite dilution: $\Lambda_0(KSO_3F) = 151.8$, $\Lambda_0(NH_4SO_3F) = 156.3$. Utilizing the transport number of the potassium ion we obtain the following ionic mobilities: $\lambda^0_{SO_3F^-} = 135$, $\lambda^0_{K^+} = 17$, and $\lambda^0_{NH_4^+} = 21$. The mobility of the potassium is considerably greater than in sulfuric acid $(\lambda^0_{K^+} = 5)$,[11] although it is not as large as would be expected from the ratio of the viscosities of the two solvents, $\eta_{H_2SO_4}/\eta_{HSO_3F} \sim 16$, if Walden's rule were valid.

For sufficiently dilute solutions the Debye–Hückel–Onsager limiting law describes the variation of equivalent conductivity with concentration[15]

$$\Lambda = \Lambda_0 - AI^{1/2} \tag{1}$$

where

$$A = \frac{2.801 \times 10^6 |z_1 z_2| q \Lambda_0}{(\epsilon T)^{3/2}(1 + q^{1/2})} + \frac{41.25(|z_1| + |z_2|)}{\eta(\epsilon T)^{1/2}}$$

and

$$q = \frac{|z_1 z_2|}{(|z_1| + |z_2|)(|z_2| t_1^0 + |z_1| t_2^0)}$$

t_1^0 and t_2^0 are the transport numbers at infinite dilution of the cation and anion, respectively, ϵ is the dielectric constant, η the viscosity of the solvent, and T the absolute temperature. Unfortunately, the dielectric constant of fluorosulfuric acid is not known so it is not possible to compare the initial slopes of the conductivity curves with that predicted by the above equation. We find, however, that by arbitrarily choosing a value of 150 for the dielectric constant of fluorosulfuric acid reasonable agreement is obtained between the experimental results and the Debye–Hückel–Onsager limiting law (Fig. 2). This value for the dielectric constant, although rather high, is perhaps not unreasonable in view of the following values: H_2O, 78 $(25°)$[16]; H_2SO_4, 100 $(25°)$[17]; 84 $(0°)$[18]; HCN, 118 $(18°)$.[15]

It is unusual, however, for the limiting law to hold up to such high concentrations and the following modified form of eq. 1 has been found to fit experimental data at moderate concentrations

$$\Lambda = \Lambda_0 - AI^{1/2}(1 + \kappa a) \tag{2}$$

where

$$\kappa a = \left(\frac{8\pi Ne^2}{1000\epsilon kT}\right)^{1/2} aI^{1/2}$$

and a is the mean diameter of the cation and anion, N is Avogadro's number, and k is Boltzmann's constant. As may be seen in Fig. 2, the experimental results agree reasonably well with the curve calculated from eq. 2 using $\epsilon = 120$ and $a = 10$. The lower value for the dielectric constant is quite reasonable and the justification for the value of a is that it has been found to account satisfactorily for deviations from ideal behavior in sulfuric acid solutions.[19]

(15) Reference 12, p. 143.
(16) Reference 12, p. 458.
(17) R. J. Gillespie and R. H. Cole, *Trans. Faraday Soc.*, **52**, 1325 (1956); R. J. Gillespie and R. F. M. White, *ibid.*, **54**, 1846 (1958).
(18) K. Fredenhagen and J. Dahmlos, *Z. anorg. allgem. Chem.*, **178**, 272 (1929).
(19) S. J. Bass, R. J. Gillespie, and J. V. Oubridge, *J. Chem. Soc.*, 837 (1960).

Other Bases.—Whether a solute behaves as an acid or a base was tested by adding a small amount of the strong base potassium fluorosulfate to a solution of the solute and noting the effect on the conductivity of the solution. If the compound is a base then the addition of more fluorosulfate ions, SO_3F^-, merely increases the conductivity of the solution. If, on the other hand, the compound is an acid then the addition of base results in the titration of the acid and a consequent decrease in the conductivity. The neutralization reaction

$$H_2SO_3F^+ + SO_3F^- \longrightarrow 2HSO_3F$$
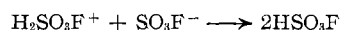
is simply the reverse of the autoprotolysis reaction. The conductivity decreases on the addition of potassium fluorosulfate to a solution of an acid since the neutralization results in the replacement of the highly conducting ion, $H_2SO_3F^+$, by the relatively poorly conducting ion, K^+. Further discussion of acid behavior and of acid–base titrations in this solvent is reserved for a later paper in this series.

The degree of ionization of a weak base can be found by comparing the concentration of base required to produce a given value of the conductivity with the concentration of a fully-ionized reference base (*e.g.*, KSO_3F) required to produce the same conductivity. This method has been used successfully for sulfuric acid solutions[20]: it assumes that the mobilities of the protonated bases are equal and that the un-ionized portion of the weak base has no effect on the conductivity. From the degree of ionization, α, at various interpolated points on the conductivity curve of a given electrolyte, values of the dissociation constant, K_b, were calculated from the relation

$$K_b = \frac{[BH^+][SO_3F^-]}{[B]} = \frac{\alpha^2 m}{1 - \alpha}$$

where B represents a weak base ionizing according to the equation

$$B + HSO_3F \rightleftharpoons BH^+ + SO_3F^-$$
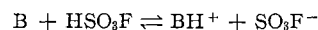
Brackets denote actual concentrations in molal units and m is the stoichiometric molal concentration of the weak base.

Organic Bases.—Conductivity measurements were made at 25° on solutions of acetic acid, benzoic acid, nitromethane, nitrobenzene, *m*-nitrotoluene, *p*-nitrochlorobenzene, *m*-nitrochlorobenzene, 2,4-dinitrotoluene, 2,4-dinitrofluorobenzene, and trinitrobenzene. The results of these measurements are given in Table IV. Acetic acid, benzoic acid, nitrobenzene, and *m*-nitrotoluene all have nearly linear conductivity–molality curves which are very similar, particularly at low concentrations, to the curves obtained for the metal fluorosulfates (Fig. 3). It is concluded that these solutes, like the metal fluorosulfates, are strong bases of the fluorosulfuric acid solvent system. The remainder of the solutes studied have lower conductivities and their conductivity curves decrease in slope with increasing concentration (Fig. 3); these solutes are therefore weak electrolytes.

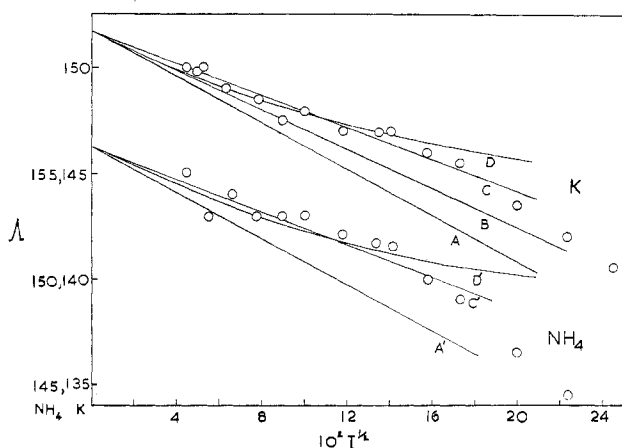(20) R. J. Gillespie and C. Solomons, *ibid.*, 1796 (1960).

Fig. 2.—Plot of equivalent conductance against the square root of the ionic strength for KSO_3F and NH_4SO_3F: A, limiting law (eq. 1), $\epsilon = 100$; B, limiting law (eq. 1), $\epsilon = 120$; C, limiting law (eq. 1), $\epsilon = 150$; D, eq. 2, $\epsilon = 120$, $a = 10$.

Dissociation constants for the incompletely ionized bases were calculated as described above. Mean values of K_b are given in Table V together with corresponding values for sulfuric acid solutions.[20,21] The value of K_b for a given base is considerably greater in fluorosulfuric acid than in sulfuric acid, showing that the former is a more strongly acidic solvent.

Potassium Sulfate and Sulfuric Acid.—Potassium sulfate gives a conductivity that is very slightly less than twice the conductivity of a solution of potassium fluorosulfate of the same concentration (Table VI). It is clear that the potassium sulfate undergoes complete solvolysis according to the equation

$$K_2SO_4 + 2HSO_3F = 2K^+ + 2SO_3F^- + H_2SO_4$$

The fact that the conductivity is very slightly less than might be expected on this basis may perhaps be attributed to an increase in the viscosity of the solution produced by the sulfuric acid or to an effect of the sulfuric acid in reducing the mobility of the fluorosulfate ion in a manner similar to that by which nonelectrolytes are known to reduce the mobility of the HSO_4^- ion in sulfuric acid.[20] Although from these results sulfuric acid appears to be a nonelectrolyte, solutions of sulfuric acid in fluorosulfuric acid were found to be weakly conducting (Table VI) and to be basic rather than acidic. The value of the basic dissociation constant K_b was found to be 10^{-4}. It is easily shown that in the presence of twice the concentration of fluorosulfate ion the extra conductivity produced by the very weak ionization of the sulfuric acid would not be observable. Sulfuric acid is therefore a very weak base whose strength is between that of 2,4-dinitrochlorobenzene and trinitrobenzene. Woolf's claim that sulfuric acid forms solutions about as conducting as those of potassium fluorosulfate[2a] is not substantiated. Our results are consistent with the earlier observation[2a] that fluorosulfuric acid behaves as a weak acid of the sulfuric acid solvent system. Thus the basic ionization of sulfuric acid in excess fluorosulfuric acid or the acid

(21) R. J. Gillespie and E. A. Robinson, *J. Chem. Soc.*, 4233 (1957).

TABLE IV

CONDUCTIVITIES OF ORGANIC BASES IN FLUOROSULFURIC ACID (25°)

10^2m	$10^4\kappa$	10^2m	$10^4\kappa$	10^2m	$10^4\kappa$
Acetic acid		Nitrobenzene		2,4-Dinitrotoluene	
0.648	13.96	0.857	21.28	0.198	4.635
1.757	42.15	1.162	28.64	0.460	8.937
2.617	61.23	1.772	42.96	1.012	16.27
3.146	71.33	2.805	66.49	1.814	24.77
3.974	89.09	43.26	98.68	2.749	32.87
0.177	4.61	62.73	135.5	3.596	39.31
0.755	18.76	79.99	167.1	4.745	47.00
1.382	34.18	98.69	199.3	6.279	56.00
2.050	50.79	120.5	234.0	8.508	66.95
2.675	66.29	154.4	282.8	10.81	76.62
3.236	80.10	*m*-Nitrotoluene		15.54	92.69
3.844	94.7	0.297	6.534	2,4-Dinitrochloro- benzene	
2.984	79.70	0.662	15.53		
6.290	152.4	1.252	29.66	0.259	3.855
7.843	183.9	1.763	41.03	0.603	6.166
10.17	228.8	2.350	53.77	1.381	9.955
11.79	258.3	2.861	64.78	2.764	14.78
13.44	287.5	3.501	78.22	4.158	18.37
Benzoic acid		4.454	101.7	5.682	21.80
0.239	7.160	5.969	130.6	8.115	26.31
0.539	15.26	7.521	158.9	9.802	28.97
1.025	27.92	8.902	184.0	12.35	32.44
1.758	47.98	10.60	213.2	2,4-Dinitrofluoro- benzene	
2.438	65.87	12.27	240.5		
3.077	82.93	*m*-Nitrochloro- benzene		1.015	8.072
2.912	75.49			1.926	11.96
3.933	99.52	0.141	4.710	3.391	16.55
5.112	125.8	0.408	10.23	4.429	19.46
6.540	156.1	0.549	13.18	5.804	22.66
8.092	187.8	1.088	23.84	6.908	25.12
9.700	218.9	2.116	41.68	1,3,5-Trinitro- benzene	
Nitromethane		3.723	65.58		
0.280	5.666	5.530	88.50	0.084	1.184
0.839	15.70	6.764	102.7	0.245	1.351
1.607	27.34	8.547	120.7	0.591	1.649
2.366	36.87	10.93	142.2	1.450	2.210
3.077	45.10	*p*-Nitrochloro- benzene		2.063	2.554
3.770	52.57			4.123	3.390
4.549	60.24	0.170	4.832	8.083	4.519
5.562	69.57	0.477	12.36	11.39	5.248
2.980	46.14	1.053	26.10	13.82	5.561
4.209	58.49	2.332	54.46		
5.368	69.31	3.688	81.92		
7.065	83.37	5.548	116.9		
8.597	95.51	8.425	165.2		
10.12	106.7	10.16	191.7		
11.64	117.2	11.53	211.1		
13.26	127.6				

ionization of fluorosulfuric acid in excess sulfuric acid may be represented by the same equation, namely

$$H_2SO_4 + HSO_3F \rightleftharpoons H_3SO_4^+ + SO_3F^-$$
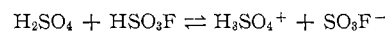
Hydrogen Fluoride.—Woolf[2b] first studied solutions of hydrogen fluoride in fluorosulfuric acid. He found that on electrolysis of solutions of HF in fluorosulfuric acid a net transport of fluorine to the cathode was obtained. This result is consistent with the formation of H_2F^+ by basic ionization of HF

$$HF + HSO_3F \rightleftharpoons H_2F^+ + SO_3F^-$$
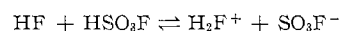
Basic behavior of HF in fluorosulfuric acid was confirmed in the present work by conductometric studies on solutions of potassium fluoride. These solutions were

TABLE V

COMPARISON OF THE IONIZATION CONSTANTS OF SOME NITRO
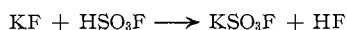COMPOUNDS IN FLUOROSULFURIC ACID AND IN SULFURIC ACID

Base	$10^2 K_b$ (HSO₃F)	$10^2 K_b$ (H₂SO₄)
Nitrobenzene	Fully ionized	1.0
m-Nitrotoluene	Fully ionized	2.3
p-Nitrochlorobenzene	76	0.4
m-Nitrochlorobenzene	7.9	...
Nitromethane	2.7	0.25
2,4-Dinitrotoluene	1.4	...
2,4-Dinitrochlorobenzene	0.16	...
2,4-Dinitrofluorobenzene	0.16	...
1,3,5-Trinitrobenzene	0.004	...

TABLE VI

CONDUCTIVITIES OF INORGANIC BASES IN FLUOROSULFURIC ACID
(25°)

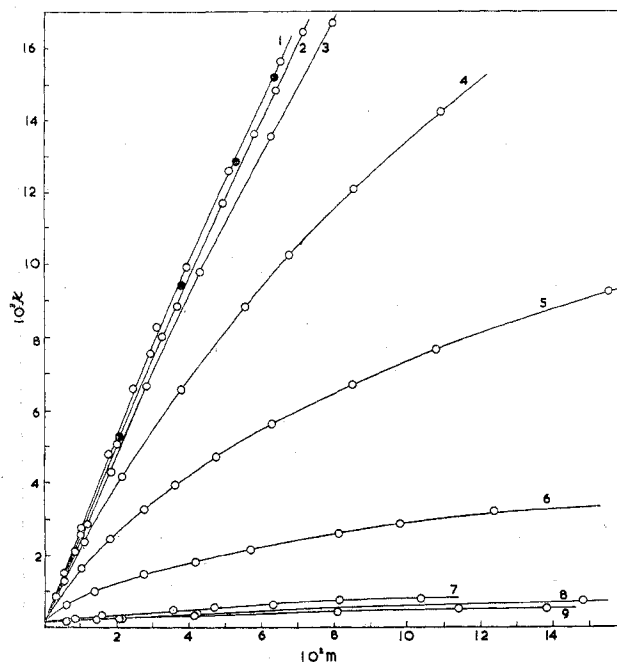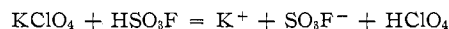| $10^2 m$	$10^4 \kappa$	$10^2 m$	$10^4 \kappa$	$10^2 m$	$10^4 \kappa$
AsF₃ (A)		AsF₃ (B)		KF	
0.556	1.125	0.445	1.404	0.625	16.33
1.131	1.179	1.622	2.342	2.038	52.08
1.782	1.317	2.167	2.808	3.777	94.46
2.493	1.519	4.225	3.826	5.306	128.7
3.261	1.709	14.81	7.730	6.364	151.9
4.331	2.037	21.87	10.75	7.916	184.8
5.392	2.419	26.41	13.25	H₂SO₄	
6.578	2.821	K₂SO₄		0.211	1.460
8.136	3.465	0.071	4.078	0.423	1.819
9.378	3.809	0.317	16.46	0.859	2.440
20.57	7.828	1.156	57.04	1.564	3.179
32.40	12.75	2.730	127.3	3.560	4.885
SbF₃		2.855	352.6	4.702	5.671
0.397	1.379	24.41	666.4	6.324	6.666
1.270	5.278	25.81	681.2	8.146	7.685
5.281	22.90	30.56	719.9	10.37	8.828
8.098	32.11	KClO₄			
		0.336	9.60		
		1.365	35.66		
		2.686	68.05		
		5.414	131.0		
		9.812	221.5		

Fig. 3.—Conductivities of some bases: 1, O, benzoic acid; ●, potassium fluoride; 2, potassium fluorosulfate; 3, nitrobenzene; 4, *m*-nitrochlorobenzene; 5, dinitrotoluene; 6, dinitrochlorobenzene; 7, sulfuric acid; 8, arsenic trifluoride (B); 9, trinitrobenzene.

found to be very slightly more conducting than solutions of potassium fluorosulfate. The experimental data are given in Table VI. Since potassium fluorosulfate can be isolated from solutions of potassium fluoride in fluorosulfuric acid,[2b] the initial reaction must involve the formation of potassium fluorosulfate and hydrogen fluoride

$$KF + HSO_3F \longrightarrow KSO_3F + HF$$

The fact that the resulting solution is very slightly more conducting than solutions of potassium fluorosulfate alone shows that HF probably behaves as a weak base.

Perchloric Acid.—Perchloric acid has been found to be a nonelectrolyte in solution in sulfuric acid and its salts undergo complete solvolysis[22]

$$KClO_4 + H_2SO_4 = K^+ + HSO_4^- + HClO_4$$

Since the conductivities of solutions of potassium perchlorate are, like those of potassium fluoride, very slightly greater than the conductivities of solutions of potassium fluorosulfate, it seems reasonable to conclude that potassium perchlorate undergoes complete solvolysis according to the equation

(22) R. J. Gillespie, *J. Chem. Soc.*, 2537 (1950).

$$KClO_4 + HSO_3F = K^+ + SO_3F^- + HClO_4$$

The fact that the conductivity is slightly greater than that of potassium fluorosulfate may reasonably be attributed to perchloric acid behaving as a very weak base

$$HClO_4 + HSO_3F = H_2ClO_4^+ + SO_3F^-$$

The difference between the conductivities of solutions of potassium perchlorate and potassium fluorosulfate is, however, so small that it could quite possibly be accounted for by small differences in the viscosities due to the presence of perchloric acid in the potassium perchlorate solutions.

Since perchloryl fluoride can be formed by heating a perchlorate with fluorosulfuric acid[23]

$$KClO_4 + 2HSO_3F = ClO_3F + H_2SO_4 + K^+ + SO_3F^-$$
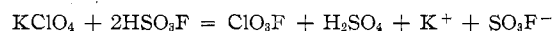
and since sulfuric acid is essentially a nonelectrolyte, and it is reasonable to assume that perchloryl fluoride would also behave as a nonelectrolyte, this would also provide an explanation of the observed conductivities of solutions of perchloric acid. However, no changes in the conductivity with time were observed, although they would be expected if the above reaction did not proceed to completion very rapidly. Moreover, a F^{19} n.m.r. spectrum of a solution of potassium perchlorate in fluorosulfuric acid did not show the characteristic spectrum of perchloryl fluoride.[24]

Woolf titrated a solution of perchloric acid with antimony pentafluoride and obtained a minimum conductivity, indicating that perchloric acid exhibits basic behavior.[5] He was reluctant to conclude that perchlo-

(23) G. Barth-Wehrenalp, *J. Inorg. Nucl. Chem.*, **2**, 266 (1956).
(24) J. Bacon, R. J. Gillespie, and J. W. Quail, *Can. J. Chem.*, **41**, 3063 (1963).

ric acid is a proton acceptor and suggested the alternative of the formation of the ClO_3^+ ion according to the equation

$$2HSO_3F + HClO_4 = ClO_3^+ + H_3O^+ + 2SO_3F^-$$
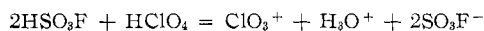
Our conductivity results are certainly not in agreement with an ionization of this kind, and if perchloric acid does behave as a proton acceptor it does so only very weakly. There is no obvious explanation for the minimum conductivity observed by Woolf, and further work is required.

Arsenic and Antimony Trifluorides.—Woolf reported that arsenic trifluoride and antimony trifluoride behave as bases in fluorosulfuric acid solutions.[2b] Our conductivity measurements (Table VI) show that arsenic trifluoride behaves as a very weak base in fluorosulfuric acid; however, the solutions are not stable and the conductivity increases somewhat with time. In one experiment (A in Table VI), conductivity measurements were made on freshly prepared solutions of arsenic trifluoride. In another experiment (B), conductivity measurements were made on solutions which had been standing for 4 days, after which time there was no further increase in the conductivity. Presumably arsenic trifluoride is behaving as a very weak base according to the equation

$$AsF_3 + HSO_3F \rightleftharpoons HAsF_3^+ + SO_3F^-$$
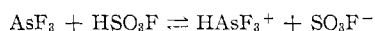
The fact that a solution which is allowed to stand for several days has a conductivity which is somewhat larger than that of a freshly prepared solution could possibly be explained by the formation of a fluorosulfate, according to the equation

$$AsF_3 + HSO_3F \rightleftharpoons AsF_2(SO_3F) + HF$$
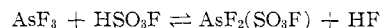
The resulting increase in conductivity could be attributed to the basic behavior of the HF produced, or to ionization of the $AsF_2(SO_3F)$

$$AsF_2(SO_3F) \rightleftharpoons AsF_2^+ + SO_3F^-$$
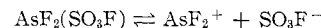
Antimony trifluoride gives solutions that are considerably more conducting than those of arsenic trifluoride; however, they are not stable and the conductivity increases relatively rapidly on standing. A few typical results on freshly prepared solutions are given in Table VI. Presumably antimony trifluoride acts as a weak base that is rather stronger than arsenic trifluoride and also undergoes further reactions in the same manner as arsenic trifluoride but rather more rapidly and extensively.