

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
MCMASTER UNIVERSITY, HAMILTON, ONTARIO**Fluorosulfuric Acid Solvent System. III. Cryoscopic Measurements**

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Received September 30, 1965

The apparatus and technique for making cryoscopic measurements in fluorosulfuric acid is described. The cryoscopic constant was determined from the freezing-point depressions produced by some nonelectrolytes and it was found to have the value 3.93 ± 0.05 deg mole⁻¹ kg. The freezing points of the system HF-SO₃ in the region of the composition HSO₃F have been studied. The freezing point of HSO₃F was found to be -88.98° . The extent of self-dissociation into SO₃ and HF at the maximum freezing point was found to be very small, but the freshly distilled acid generally contains a very small excess of SO₃. The self-dissociation equilibrium constant $K = [\text{SO}_3][\text{HF}]$ probably has a value of less than 3×10^{-7} . Both SO₃ and HF are shown to behave as nonelectrolytes in solution in HSO₃F. Metal fluorosulfates and benzoic acid were found to behave as simple binary electrolytes. The extent of ionization of some nitro compounds has been determined from their freezing-point depressions.

Introduction

The two previous papers in this series reported mainly the results of electrical conductivity measurements on solutions in fluorosulfuric acid.^{1,2} In extensive studies of solutions in sulfuric acid it has been found that it is very important to obtain both cryoscopic and conductometric data in order to elucidate completely the mode of ionization of solutes.³ We have therefore now applied the cryoscopic method to solutions in fluorosulfuric acid, and this paper describes the experimental technique and the determination of the cryoscopic constant and reports the results of cryoscopic measurements on some simple electrolytes. The application of cryoscopy, conductivity, and other experimental techniques to the elucidation of the ionization of more complex electrolytes will be described in following papers.

Experimental Section

The cryoscopic measurements were made by an adaption of the method described by Rossini and co-workers.^{4,5} The cryoscope (Figure 1) was a double-walled vessel and the annular space between the walls (A) could be evacuated to any required pressure down to 10^{-4} mm. The walls of the annular space were silvered except for narrow vertical strips on opposite sides which were left clear so that the contents could be observed. Temperatures were measured to 0.001° with a platinum resistance thermometer (B) used in conjunction with a Mueller resistance bridge. A Teflon sleeve fitted around the thermometer at D allowed a tight fit of the thermometer into a glass sleeve fitted with a male B 14 ground joint which was inserted into the female part of the joint I in the cryoscope head. The thermometer calibration was checked periodically by determining its resistance at the triple point of water using a Trans-Sonics Inc. "Equiphase cell." The glass or nichrome alloy stirrer (C) was operated through a Teflon seal at E by an electric windshield-wiper motor.

The cryoscope was first dried by passing a slow stream of dry air in through G and out *via* an "Anhydrone" guard tube at-

tached at F for at least 1 hr. About 150 g of fluorosulfuric acid was distilled into the weight dropper (Figure 1), which was then attached to the cryoscope at F, and dry air was passed through for another 0.5 hr, leaving now by a guard tube attached to J. Another guard tube was attached to the weight dropper at K and the acid allowed to run into the cryoscope. The weight of acid in the cryoscope was determined by difference. The exits F and G were now closed and for the remainder of the experiment a very slow stream of dry air was passed in at H and out through the sleeve at E. Additions of powdered solid and liquid solutes were made through F using suitable weight droppers.

Freezing points were determined as follows: a large dewar flask containing liquid air was placed in position around the cryoscope and the temperature in the cryoscope was allowed to fall to about -70° . The annular space A was then evacuated to give a cooling rate of between 0.2 and $0.5^\circ/\text{min}$. The solution was allowed to supercool about 2° and then freezing was initiated by introducing a small piece of platinum wire which had been cooled in liquid air. The temperature of the solution then rose rapidly and reached a maximum value in about 5 min. Measurements of the resistance of the thermometer were made at regular intervals of 30 sec or 1 min starting at the time when the temperature was still several degrees above the expected freezing point and they were continued for about 20-25 min after freezing had occurred. It has been shown that the true freezing point of the solution can be obtained by extrapolating the freezing-point curve back to its intersection with the cooling curve before freezing is initiated provided the temperature head (*i.e.*, the difference in temperature between the solution and the cooling bath) is large compared with the amount of supercooling.⁴ A temperature head of at least 50° and a supercooling of not more than 5° has been shown to be satisfactory.⁴ In the present work the temperature head was 100° and the amount of supercooling was generally only 2° and never more than 4° . Taylor and Rossini have described a geometrical method of extrapolating the freezing curve to obtain the true freezing point.⁵ We found that simple visual extrapolation of the freezing-point curve gave results that agreed within $\pm 0.005^\circ$ with the values obtained by the Taylor and Rossini method and that separate freezing points on the same solution were also reproducible to within the same limits. We therefore used the simple visual extrapolation in almost all cases.

Conductivity experiments were carried out in the manner described previously.¹

Fluorosulfuric acid was purified as described in part I¹ and was distilled directly into the weight dropper or conductivity cell. Sulfur trioxide was prepared by distillation from Baker and Adamson Sulfan B to which K₂S₂O₈ had been added. The alkali metal fluorosulfates were prepared as described in part I.¹ Potassium fluorosulfate was also prepared by addition of fluorosulfuric acid to a concentrated solution of potassium hydroxide at 0° . The product was recrystallized from ice-cold water and

(1) J. Barr, R. J. Gillespie, and R. C. Thompson, *Inorg. Chem.*, **3**, 1149 (1964).

(2) R. C. Thompson, J. Barr, R. J. Gillespie, J. Milne, and R. A. Rothenbury, *ibid.*, **4**, 1641 (1965).

(3) R. J. Gillespie and E. A. Robinson, *Advan. Inorg. Chem. Radiochem.*, **1**, 386 (1959).

(4) B. J. Mair, A. R. Glasgow, and F. D. Rossini, *J. Res. Natl. Bur. Std.*, **26**, 591 (1941).

(5) W. J. Taylor and F. D. Rossini, *ibid.*, **32**, 197 (1944).

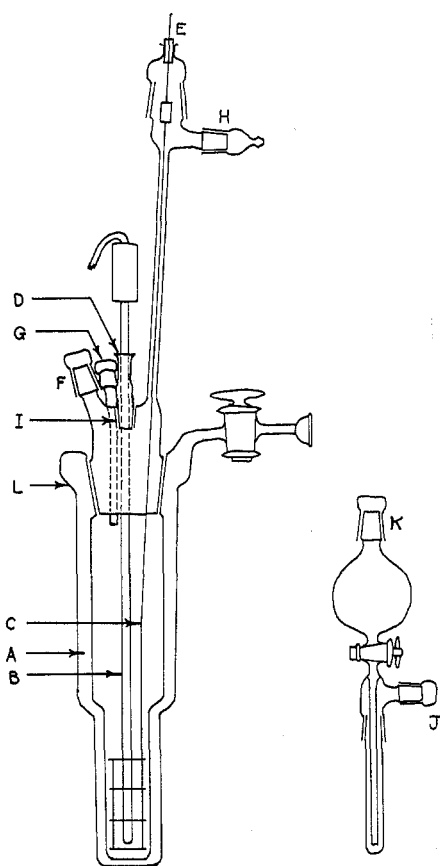


Figure 1.—The cryoscope and weight dropper.

then washed with acetone and ether and stored over phosphorus pentoxide. Peroxydisulfuryl difluoride was prepared by the method of Dudley and Cady.⁶ Disulfuryl difluoride was prepared as described by Gillespie and Rothenbury.⁷ Matheson's anhydrous hydrogen fluoride was used directly. The nitro compounds and benzoic acid were purified as described in part I.¹ Methyl sulfonyl fluoride and 2,5-dimethylbenzene sulfonyl fluoride were Eastman Grade chemicals. Purified grade potassium fluoride was dried in an oven at 120° for 2 days.

For the cryoscopy and conductivity of hydrogen fluoride, sulfur trioxide, peroxydisulfuryl difluoride, and disulfuryl difluoride, solute additions were made in the form of concentrated solutions in fluorosulfuric acid. Other solutes were added as the pure substance.

Results and Discussion

The Cryoscopic Constant.—As the heat of fusion of fluorosulfuric acid is not known it was necessary to establish the cryoscopic constant by measuring the freezing-point depression produced by some nonelectrolytes. It is difficult to find true nonelectrolytes of the fluorosulfuric acid solvent system but disulfuryl difluoride, $S_2O_5F_2$, peroxydisulfuryl difluoride, $S_2O_6F_2$, and sulfur trioxide were found to increase the conductivity of the solvent by only a negligible amount (Table I). A comparable increase in the conductivity at each addition (10^{-5} ohm⁻¹ cm⁻¹), presumably arising from the absorption of atmospheric moisture, was observed when a check run was made in which an empty dropper was used. In this run an addition was simulated as follows: the cell was opened, an empty dropper

TABLE I
SPECIFIC CONDUCTANCES OF $S_2O_5F_2$, $S_2O_6F_2$, AND SO_3

| $S_2O_5F_2$ | | $S_2O_6F_2$ | | SO_3 | |
|-------------|---|-------------|---|---------|---|
| 10^2m | 10^4k , ohm ⁻¹ cm ⁻¹ | 10^2m | 10^4k , ohm ⁻¹ cm ⁻¹ | 10^2m | 10^4k , ohm ⁻¹ cm ⁻¹ |
| 0.00 | 1.358 | 0.00 | 1.378 | 0.00 | 1.248 |
| 2.48 | 1.385 | 0.86 | 1.529 | 7.28 | 1.333 |
| 5.37 | 1.397 | 1.63 | 1.645 | 18.22 | 1.423 |
| 6.86 | 1.413 | 2.44 | 1.772 | 28.25 | 1.450 |
| 8.85 | 1.443 | 3.18 | 1.953 | 48.87 | 1.533 |
| 10.84 | 1.482 | 3.84 | 2.216 | 65.51 | 1.659 |
| | | | | 89.32 | 1.726 |

was inserted and withdrawn, the cell was closed and shaken, and the conductance was measured.

The results of cryoscopic measurements on $S_2O_5F_2$ and $S_2O_6F_2$ are shown in Table II and Figure 2. The

TABLE II
FREEZING-POINT DEPRESSIONS

| 10^2m | θ , °C | 10^2m | θ , °C |
|---------------------------------------|---------------|--------------------------|---------------|
| $S_2O_5F_2$ | | $CsSO_3F$ | |
| F.p. of solvent | -89.007° | F.p. of solvent | -88.999° |
| 0.28 | 0.017 | 3.40 | 0.243 |
| 0.82 | 0.034 | 6.43 | 0.483 |
| 1.53 | 0.061 | 10.38 | 0.822 |
| 2.08 | 0.076 | 12.93 | 1.042 |
| 2.69 | 0.109 | | |
| 3.22 | 0.126 | | |
| $S_2O_6F_2$ | | $RbSO_3F$ | |
| F.p. of solvent | -88.996° | F.p. of solvent | -88.999° |
| 0.88 | 0.032 | 6.04 | 0.443 |
| 1.93 | 0.074 | 11.46 | 0.903 |
| 3.85 | 0.152 | 15.28 | 1.272 |
| 5.18 | 0.203 | 18.90 | 1.621 |
| F.p. of solvent | -88.994° | 22.34 | 1.956 |
| 5.56 | 0.216 | | |
| KSO_3F | | $LiSO_3F$ | |
| F.p. of solvent | -88.999° | F.p. of solvent | -88.983° |
| 5.25 | 0.382 | 7.21 | 0.547 |
| 13.36 | 1.081 | 13.0 | 1.021 |
| 21.49 | 1.825 | 23.8 | 1.927 |
| F.p. of solvent | -89.026° | $C_6H_5CO_2H$ | |
| 5.11 | 0.379 | F.p. of solvent | -89.134° |
| 18.97 | 1.656 | 3.07 | 0.232 |
| 26.29 | 2.450 | 7.31 | 0.546 |
| F.p. of solvent | -89.005 | 12.64 | 0.967 |
| 0.54 | 0.030 | 18.00 | 1.390 |
| 1.26 | 0.081 | 22.50 | 1.844 |
| 1.82 | 0.122 | | |
| 2.46 | 0.168 | | |
| 3.16 | 0.223 | | |
| 3.68 | 0.266 | | |
| KF | | Methyl sulfonyl fluoride | |
| F.p. of solvent | -88.987° | F.p. of solvent | -88.988° |
| 0.77 | 0.065 | 2.48 | 0.100 |
| 1.69 | 0.157 | 5.23 | 0.211 |
| 2.68 | 0.275 | 7.80 | 0.312 |
| 4.09 | 0.440 | 10.41 | 0.413 |
| 6.45 | 0.703 | | |
| 8.84 | 1.000 | | |
| 2,4-Dinitrotoluene | | 1,3,5-Trinitrobenzene | |
| F.p. of solvent | -89.007° | F.p. of solvent | -88.998° |
| 1.07 | 0.063 | 1.76 | 0.060 |
| 2.25 | 0.129 | 3.55 | 0.129 |
| 3.37 | 0.189 | 5.44 | 0.210 |
| 4.88 | 0.279 | 7.62 | 0.306 |
| 8.57 | 0.448 | 10.48 | 0.421 |
| | | 13.47 | 0.567 |
| | | 17.70 | 0.789 |
| 2,5-Dimethylbenzene sulfonyl fluoride | | | |
| F.p. of solvent | -89.005° | | |
| 1.92 | 0.073 | | |
| 3.66 | 0.133 | | |
| 5.48 | 0.197 | | |
| 7.24 | 0.261 | | |
| 9.10 | 0.325 | | |

(6) F. B. Dudley and G. H. Cady, *J. Am. Chem. Soc.*, **79**, 513 (1957).

(7) R. J. Gillespie and R. A. Rothenbury, *Can. J. Chem.*, **42**, 416 (1964).

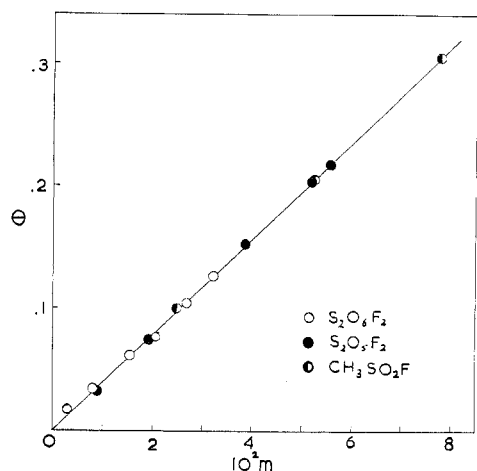


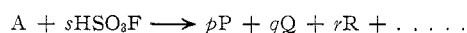
Figure 2.—Freezing-point depressions produced by some nonelectrolytes; θ , freezing-point depression ($^{\circ}\text{C}$); m , molality of solute.

results for SO_3 are discussed below. The experimental points for $\text{S}_2\text{O}_5\text{F}_2$ and $\text{S}_2\text{O}_6\text{F}_2$ lie on a good straight line whose slope gives a value of the cryoscopic constant of $3.93 \pm 0.05 \text{ deg mole}^{-1} \text{ kg}$. This value was confirmed in various ways as described below.

Calculation of ν .—The freezing-point depression ν produced by any solute is given by the expression

$$\theta = k_f \Sigma m_i$$

where k_f is the cryoscopic constant and Σm_i is the total molality of all the solute species. This equation is only approximate, as it ignores the variation of the heat of fusion with temperature and any nonideal behavior of the solution. If 1 mole of a solute A reacts with s moles of the solvent to produce p moles of a product P, q moles of a product Q, etc., *i.e.*



where $p + q + r + \dots = \nu$, then

$$\Sigma m_i = \frac{\nu m}{1 - 0.1ms}$$

where m is the stoichiometric molality of the solute A, since the molecular weight of HSO_3F is 100. Hence

$$\theta = \frac{k_f \nu m}{1 - 0.1ms}$$

and therefore

$$\nu = \frac{\theta}{3.93m} (1 - 0.1ms) \quad (1)$$

The Solutes Sulfur Trioxide, Hydrogen Fluoride, and Potassium Fluoride.—Hydrogen fluoride was found to produce a small initial rise in the freezing point before it gave a depression (Table III). The most probable explanation is that the solvent contains a very small excess of sulfur trioxide which is removed by the added HF according to the equation

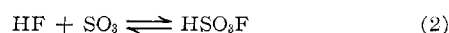


TABLE III
FREEZING POINTS OF SOLUTIONS OF HF AND SO_3

| $10^2 m^{\text{HF}}$ | $-T_f$, $^{\circ}\text{C}$ | $10^2 m^{\text{HF(SO}_3)}$ | $10^2 m^{\text{HF}}$ | T_f , $^{\circ}\text{C}$ | $10^2 m^{\text{HF(SO}_3)}$ |
|----------------------|--------------------------------|----------------------------|------------------------|-------------------------------|-------------------------------------|
| 0.00 | 89.000 | 0.50 (SO_3) | 0.00 | 88.996 | 0.40 (SO_3) |
| 0.48 | 88.988 | 0.02 (SO_3) | 0.35 | 88.985 | 0.05 (SO_3) |
| 1.21 | 89.013 | 0.71 | 0.74 | 89.000 | 0.34 |
| 1.77 | 89.030 | 1.27 | 1.09 | 89.010 | 0.69 |
| 2.21 | 89.044 | 1.71 | 1.58 | 89.031 | 1.18 |
| 2.65 | 89.058 | 2.15 | 2.13 | 89.042 | 1.73 |
| 3.30 | 89.080 | 2.80 | 2.83 | 89.071 | 2.43 |
| 3.90 | 89.100 | 3.40 | 3.84 | 89.112 | 3.44 |
| 0.00 | 88.996 | 0.40 (SO_3) | 0.00 | 89.005 | 0.65 (SO_3) ^a |
| 0.72 | 88.991 | 0.32 | 2.48 | 89.055 | 1.83 |
| 1.16 | 89.014 | 0.76 | | | |
| 1.85 | 89.036 | 1.45 | $10^2 m^{\text{SO}_3}$ | | |
| 2.60 | 89.064 | 2.20 | 0.58 | 89.034 | 1.25 |
| | | | 2.48 | 89.005 | 0.65 (SO_3) |
| 0.00 | 89.007 | 0.70 (SO_3) | 5.24 | 89.108 | 3.41 (SO_3) |
| 2.43 | 89.047 | 1.73 | 8.63 | 89.247 | 6.80 (SO_3) |
| 3.01 | 89.068 | 2.31 | 10.68 | 89.335 | 8.85 (SO_3) |
| 4.25 | 89.099 | 4.55 | 13.85 | 89.464 | 12.02 (SO_3) |

^a In this experiment one addition of HF was made followed by six additions of SO_3 .

By assuming that the only impurity in the solvent is SO_3 and that the initial freezing point is therefore a measure of the SO_3 concentration it was found possible to fit all the observed points for both HF and SO_3 quite satisfactorily to a common freezing-point curve which has two branches each of slope $3.93 \text{ deg mole}^{-1} \text{ kg}$ and a very sharp maximum (Figure 3). Molalities of HF and SO_3 corrected for the amount of SO_3 initially present (m^c) are given in column 3 of Table III. Extrapolation of the two linear branches of the curve until they intersect gives a value of -88.980° for the hypothetical freezing point of undissociated HSO_3F . It seems unlikely from the data in Figure 3 that the actual freezing-point maximum is more than 0.004° lower than this, indicating a total molality of self-dissociation products of only $0.001 m$ and hence a self-dissociation constant $K = [\text{HF}][\text{SO}_3] < 3 \times 10^{-7}$.

The freezing points of some of the HF solutions at the highest concentrations studied are a little high. This probably results from loss of HF by vaporization from the relatively concentrated solution in HSO_3F that was made up for addition to the cryoscope by means of the weight dropper.

We conclude that both sulfur trioxide and hydrogen fluoride behave as monomeric nonelectrolytes in fluorosulfuric acid. The cryoscopic measurements do not appear to be accurate enough to detect the very slight ionization of HF as a base that was postulated in order to explain our earlier observation¹ that the conductivity of KF solutions is very slightly greater than that of KSO_3F solutions.

The conclusion that sulfur trioxide is a nonelectrolyte in fluorosulfuric acid does not necessarily imply that it does not react with the solvent. Indeed previous Raman spectral studies have shown clearly that there is a reaction between sulfur trioxide and the solvent to form fluorodisulfuric acid⁸



(8) R. J. Gillespie and E. A. Robinson, *Can. J. Chem.*, **40**, 675 (1962).

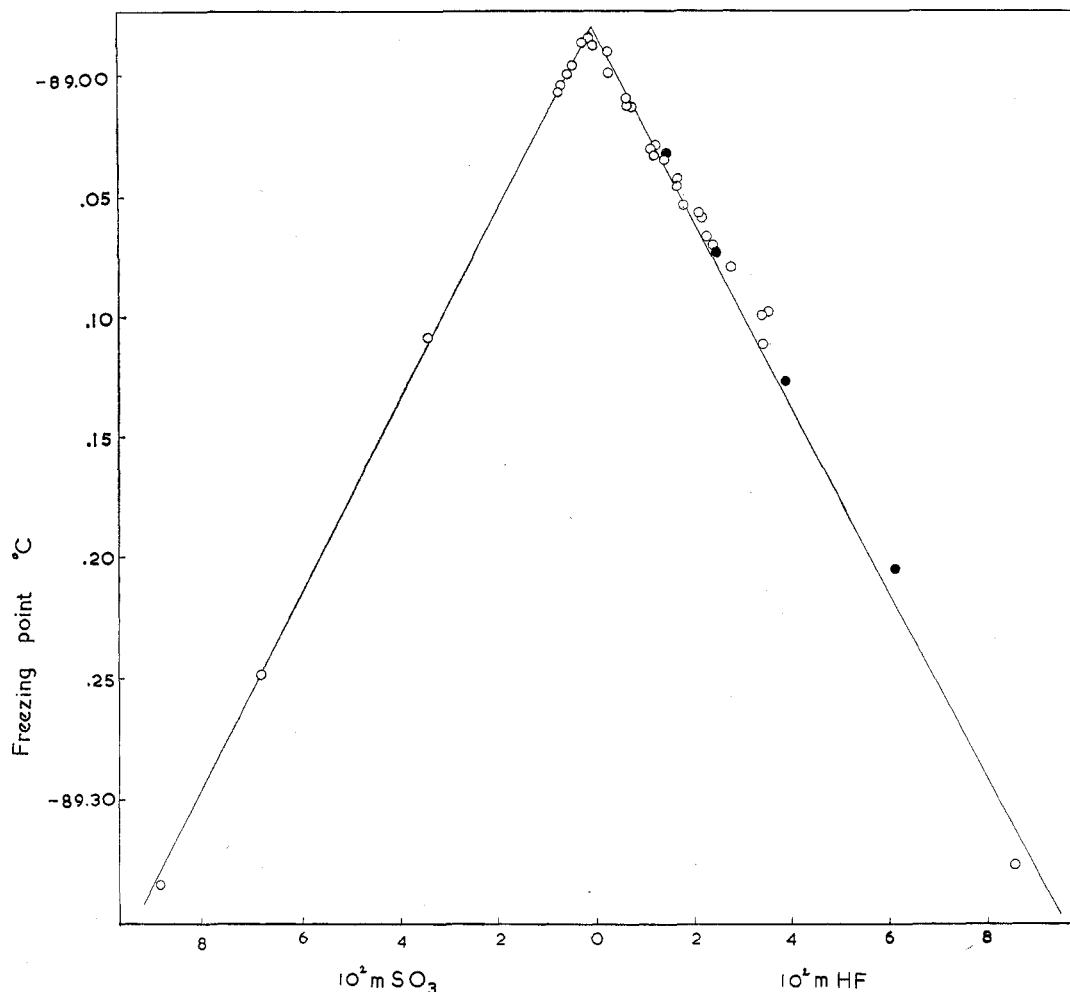
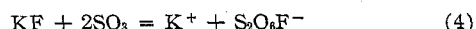


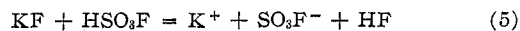
Figure 3.—Freezing points of the HF-SO₃ system in the region of the maximum at the composition HSO₃F: ●, KF-KSO₃F.

We must conclude that, in contrast to H₂S₂O₇ in H₂SO₄,⁹ HS₂O₆F is not a sufficiently strong acid to ionize to any detectable amount in solution in HSO₃F.

Potassium fluoride gave an almost linear freezing-point depression curve but it did not quite pass through the origin, presumably because of reaction with excess SO₃ in the solvent according to the equation



Thus initially KF would cause no depression of the freezing point. Extrapolation of the observed curve to the concentration axis gave a concentration of SO₃ of 0.0025 *m*, which agrees with the amount predicted from the initial freezing point of the acid. The molalities of potassium fluoride were corrected for the amount of SO₃ used up in this reaction and then values of ν were calculated. The mean value of 2.9 (Table V) indicates that potassium fluoride ionizes in the following manner



By subtracting the freezing-point depression for potassium fluorosulfate from that for potassium fluoride at each concentration a freezing-point curve for HF was

obtained which agreed well with that obtained directly (Figure 3).

The ¹⁹F nmr spectrum of a solution of potassium fluoride in fluorosulfuric acid was examined at several temperatures between 25 and -83°. At 25° a single rather broad peak was observed at approximately 222 ppm to high field of the solvent resonance. As the temperature was lowered this peak broadened further until at -50° it could not be observed above the baseline noise, but at -83° two relatively sharp peaks appeared, one at approximately 222 ppm and a very small peak at approximately 206 ppm to high field of the solvent peak. The larger peak is almost certainly due to HF, while the very small peak is probably due to a small amount of silicon tetrafluoride produced by attack on the glass. The chemical shift between the two peaks is 16 ppm, while the chemical shift between the ¹⁹F resonances in the pure liquids HF and SiF₄ is reported to be 26 ppm.¹⁰ The difference could easily be accounted for by medium effects. The solution was much more concentrated than that used in the conductometric and cryoscopic experiments in which no reaction of the solution with the glass was noticed. The collapse of the two peaks and their reappearance as a single broad peak as the temperature is raised shows

(9) S. J. Bass, R. J. Gillespie, and E. A. Robinson, *J. Chem. Soc.*, 821 (1960).

(10) H. S. Gutowsky and C. J. Hoffman, *J. Chem. Phys.*, **19**, 1259 (1951).

that fluorine exchange occurs between HF and SiF₄ in these solutions.

The Freezing Point of Fluorosulfuric Acid.—The freshly distilled acid generally had a freezing point in the range -88.99 to -89.01° . In view of the results obtained above with the solute HF we conclude that this freshly distilled acid contains a very small and somewhat variable concentration of SO₃, in general less than $0.01 m$. This conclusion is confirmed by the results of the experiments with metal fluorosulfates described later. Mair, Glasgow, and Rossini⁴ have given a method for the determination of the concentration of impurities in a solvent and thus the freezing point of the pure solvent. When the total molality of the impurities is small it may be expressed by

$$\Sigma m_i = \frac{1-r}{rk_f} (T - T_r) \quad (6)$$

where r is the fraction of solvent crystallized, k_f is the cryoscopic constant, T is the temperature at which crystallization begins, and T_r is the temperature when the fraction r is frozen. The freezing point of the pure solvent T_0 is then given by

$$T_0 = T + k_f \Sigma m_i \quad (7)$$

In the case where one or more of the impurities represses the solvent self-dissociation than we obtain T^* , the freezing point of the hypothetical undissociated acid, from the equation

$$T^* = T + k_i \Sigma m_i \quad (8)$$

Table IV gives the results of an experiment in which a sample of fluorosulfuric acid was allowed to freeze until it became completely solid. As it is very likely the only important impurity is SO₃, and this represses the solvent self-dissociation, values of T^* were computed from eq 8 at $r = 1/3, 1/2,$ and $3/4$ and a mean value of -89.977° was obtained. This is in excellent agreement with the value of -88.980° obtained above.

TABLE IV
DETERMINATION OF FREEZING POINT OF PURE HSO₃F

| r | $T_r, ^\circ\text{C}$ | m_i | $T^*, ^\circ\text{C}$ |
|-----|-----------------------|--------|-----------------------|
| 0 | -88.987 | ... | ... |
| 1/3 | -88.992 | 0.0025 | -88.977 |
| 1/2 | -88.999 | 0.0030 | -88.975 |
| 3/4 | -89.011 | 0.0021 | -88.979 |

The difference between the freezing point of the pure acid T_0 and the hypothetical freezing point of the undissociated acid T^* is less than the possible thermometer calibration errors; thus a value of -88.98° may be given for both T_0 and T^* .

Metal Fluorosulfates and Benzoic Acid.—It was shown in part I by conductometric studies that alkali metal fluorosulfates and carboxylic acids behave as simple binary electrolytes. The freezing points of solutions of lithium, potassium, rubidium, and cesium fluorosulfates and benzoic acid are given in Table III and Figure 4. The experimental points for these solutes fall very close to a common curve which between 0.01

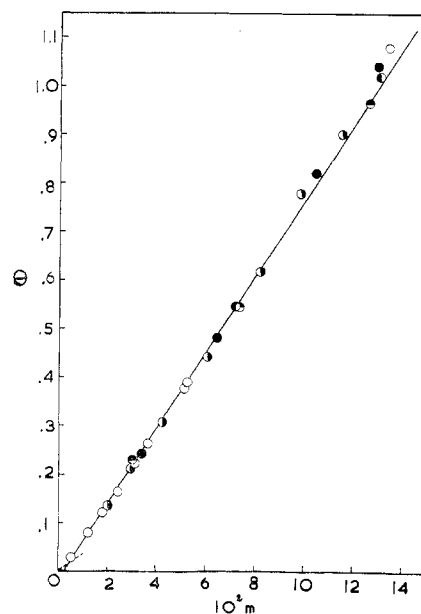
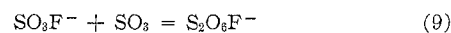


Figure 4.—Freezing-point depression produced by the alkali metal fluorosulfates and benzoic acid: O, KSO₃F; ●, LiSO₃F; ●, CsSO₃F; ◐, RbSO₃F; ◑, C₆H₅CO₂H; θ, freezing-point depression ($^\circ\text{C}$); m , molality of solute.

and $0.10 m$ is linear and has a slope of 2×3.93 , *i.e.*, $\nu = 2.0$. This result confirms that these solutes behave as fully ionized binary electrolytes and also provides further confirmation of the value of the cryoscopic constant. The straight line does not pass through the origin and although there is only one experimental point below $0.01 m$ it is clear that the freezing-point curve has a low initial slope. This can be attributed to reaction of the fluorosulfate ion with the small excess of sulfur trioxide that we believe to be present in the acid.



Thus initially the freezing-point curve for these solutes has a slope of 3.93 , corresponding to the addition of only one new particle to the solution. When all the SO₃ has been removed the curve then has the expected slope corresponding to $\nu = 2$. The concentration of sulfur trioxide initially present in the solvent can be found from the intersection of the extrapolated portions of the initial curve corresponding to $\nu = 1$ and the final curve corresponding to $\nu = 2$. The sulfur trioxide concentration in the solvent obtained in this manner from the results for potassium fluorosulfate at low concentrations was found to be $0.0055 m$. This agrees well with the concentration of SO₃ of $0.0065 m$ which may be calculated from the initial freezing point of the acid.

Above $0.01 m$ the slope of the freezing-point curves for these electrolytes increases to a value greater than that for an ideal binary electrolyte. This is quite analogous to the behavior of simple hydrogen sulfates in sulfuric acid, and it has been interpreted as indicating that interionic forces are relatively small; at higher concentrations their effects are completely masked by ion-solvent interaction. Presumably the observed increase in the slope of the freezing-point curves for fluorosul-

fates in fluorosulfuric acid may similarly be attributed to ion-solvent interaction. Unfortunately our measurements are not extensive enough to allow us to compare the different extents of solvation of different electrolytes as has been done in the case of sulfates in sulfuric acid.¹¹

Sulfonyl Fluorides.—The results of the cryoscopic measurements are given in Table II. Methyl sulfonyl fluoride gave a freezing-point depression curve identical with that of $S_2O_6F_2$ and $S_2O_5F_2$ (Figure 2) and is clearly therefore a nonelectrolyte. 2,5-Dimethylbenzene sulfonyl fluoride gave a freezing-point depression slightly less than that of a nonelectrolyte. The reason for this is not entirely clear but it may be due to nonideality associated with the very limited solubility of this compound in fluorosulfuric acid. Neither of the sulfonyl fluorides was completely stable in solution in fluorosulfuric acid as the originally colorless solutions slowly darkened if allowed to stand at room temperature.

Nitro Compounds.—The results of the cryoscopic measurements are given in Table III. The depression produced by the first addition of trinitrobenzene was somewhat less than that expected for a nonelectrolyte; thereafter the freezing-point curve was found to have a slope slightly greater than that for an ideal nonelectrolyte that increased somewhat with increasing concentration. The reason for the initial low depression is not clear. The fact that eventually the freezing-point curve has a slope slightly greater than that for an ideal nonelectrolyte is consistent with the slight degree of ionization found previously by conductometric measurements¹ and the increasing slope with increasing concentration may be attributed to nonideal behavior such as has been previously found in sulfuric acid and which it has been supposed results largely from the large size of the solute and the consequent nonideal entropy of mixing with the solvent.¹¹

(11) S. J. Bass, R. J. Gillespie, and J. V. Oubridge, *J. Chem. Soc.*, 837 (1960).

2,4-Dinitrotoluene gives a depression that is greater than that for a nonelectrolyte. Values of ν calculated from the cryoscopic results are given in Table V. They indicate that this solute is extensively ionized, presumably according to the equation



The equilibrium constant for this reaction calculated from the ν values is also given in Table V. The same value was obtained previously from conductometric studies.¹ This excellent agreement may be partly fortuitous as there is a difference of 115° between the temperatures at which the cryoscopic and conductometric measurements are made.

TABLE V
VALUES OF ν AND K
2,4-Dinitrotoluene

| $10^2 m$ | $\theta, ^\circ C$ | ν | $10^2 K$ |
|----------|--------------------|-------|----------|
| 2 | 0.117 | 1.49 | 1.0 |
| 4 | 0.227 | 1.45 | 1.5 |
| 6 | 0.329 | 1.40 | 1.6 |
| 8 | 0.420 | 1.34 | 1.4 |
| 10 | 0.512 | 1.30 | 1.5 |
| | | Mean | 1.4 |

KF

| $10^2 m^a$ | $\theta, ^\circ C$ | ν |
|------------|--------------------|-------|
| 2 | 0.226 | 2.88 |
| 4 | 0.453 | 2.88 |
| 6 | 0.681 | 2.89 |
| 8 | 0.923 | 2.94 |

^a Corrected for the KF used up initially in reaction with excess SO_3 .

Acknowledgments.—We thank the Petroleum Research Fund of the American Chemical Society and the United States Air Force Office of Scientific Research for generous financial assistance. We also thank the Ontario Research Foundation for the award of a fellowship (to R. C. T.) and the National Research Council of Canada for the award of a studentship (to J. B. M.).

CONTRIBUTION FROM THE WESTERN RESEARCH CENTER,
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Structure of the Tetrafluorochlorate(III) Anion, ClF_4^-

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Received November 5, 1965

Infrared and conductivity measurements show that $MClF_4$ (where M is NO, Rb, or Cs) is ionic in the solid state and in solution, respectively. A square-planar structure (point group D_{4h}) is assigned to the ClF_4^- anion in $Rb^+ClF_4^-$ and $Cs^+ClF_4^-$. For the ClF_4^- anion in $NO^+ClF_4^-$, the low-temperature infrared measurement indicates a lower symmetry.

Introduction

While the existence of $MClF_4$ (where M is NO, K, Rb, or Cs) is well known,¹⁻⁴ no reports on the ionic

(1) L. B. Asprey, J. L. Margrave, and M. E. Silverthorn, *J. Am. Chem. Soc.*, **83**, 2955 (1961).

(2) D. H. Kelley, B. Post, and R. W. Mason, *ibid.*, **85**, 307 (1963).

character of the $NOF-ClF_3$ adduct and on the structure of the ClF_4^- anion have been published. As-

(3) E. Whitney, R. MacLaren, C. Fogle, and T. Hurley, *ibid.*, **86**, 2583 (1964).

(4) E. Whitney, R. MacLaren, T. Hurley, and C. Fogle, *ibid.*, **86**, 4340 (1964).