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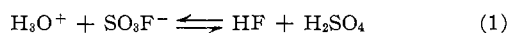
## The Fluorosulfuric Acid Solvent System. IV. The Solutes Water and Potassium Nitrate

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It is shown that in solutions of water in fluorosulfuric acid protonation and partial hydrolysis occur, and the following equilibrium is set up:  $\text{H}_3\text{O}^+ + \text{SO}_3\text{F}^- \rightleftharpoons \text{HF} + \text{H}_2\text{SO}_4$ . Values for the equilibrium constant of this reaction have been obtained at 25, 0, and  $-78.5^\circ$ . Potassium nitrate ionizes according to the equation:  $\text{KNO}_3 + 3\text{HSO}_3\text{F} = \text{K}^+ + \text{NO}_2^+ + \text{H}_3\text{O}^+ + 3\text{SO}_3\text{F}^-$ . A general method is outlined for interpreting the results of conductivity measurements on complex electrolytes such as potassium nitrate that ionize to produce water. A technique is described for the measurement of conductivities at  $-78.5^\circ$ .

The equilibrium  $\text{HF} + \text{H}_2\text{SO}_4 = \text{HSO}_3\text{F} + \text{H}_2\text{O}$  has been studied previously by Traube and Reubke<sup>1</sup> and by Lange.<sup>2</sup> They reported that the law of mass action is not obeyed in this system. Gillespie and Robinson<sup>3</sup> showed that the Raman spectra of solutions of water in fluorosulfuric acid contained several lines characteristic of the fluorosulfate ion and a line at  $910\text{ cm}^{-1}$  that may be attributed to sulfuric acid. They proposed that water is protonated but that some hydrolysis of fluorosulfuric acid also occurs; *i.e.*, the equilibrium is set up



The present work fully confirms this conclusion. After an initially low slope, the freezing-point-depression curve for water (Table I and Figure 1) becomes almost linear and has a slope that is very close to that corresponding to  $\nu = 2$ . Similar behavior has been found previously for metal fluorosulfates,<sup>4</sup> and the initial low slope was attributed to reaction of the solute with the small excess of  $\text{SO}_3$  present in the solvent. In this case the initial reaction is expected to be



which, if it went to completion, would give a zero slope for the freezing-point curve until all the  $\text{SO}_3$  had been removed. Extrapolation to the concentration axis of the linear portion of the observed curve for water gives an  $\text{SO}_3$  concentration of  $0.003\text{ m}$  which agrees well with the amount of  $0.0035\text{ m}$  which can be estimated from the initial freezing point of  $-88.994^\circ$ .<sup>4</sup>

We conclude that water ionizes to produce two particles in agreement with equilibrium 1. However, the position of the equilibrium cannot be obtained from the cryoscopic results.

The conductivities of solutions of water were measured at 25, 0, and  $-78.5^\circ$  and are given in Table II and Figure 2. For purposes of comparison conductivities of solutions of  $\text{KSO}_3\text{F}$  were also measured at 0 and  $-78.5^\circ$ , and the results of these measurements are also

given in Table II. Values of the conductivities of potassium fluorosulfate solutions at  $25^\circ$  have been reported previously.<sup>5</sup> The conductivities of solutions of water are appreciably less than those of potassium fluorosulfate at all three temperatures indicating that

TABLE I  
FREEZING-POINT DEPRESSIONS ( $\theta$ ) FOR SOLUTIONS OF WATER<sup>a</sup>

$10^2m$	$\theta$
0.32	0.010°
0.75	0.038
1.14	0.066
1.53	0.095
1.98	0.129
2.57	0.177

<sup>a</sup> Fp of solvent  $-88.994^\circ$ .

TABLE II  
CONDUCTIVITIES OF SOLUTIONS OF WATER AND  
POTASSIUM FLUOROSULFATE

$\text{H}_2\text{O}$				$\text{KSO}_3\text{F}$	
$10^2m$	$10^4\kappa$ , $\text{ohm}^{-1}\text{ cm}^{-1}$	$10^2m$	$10^4\kappa$ , $\text{ohm}^{-1}\text{ cm}^{-1}$	$10^2m$	$10^4\kappa$ , $\text{ohm}^{-1}\text{ cm}^{-1}$
$25^\circ$				$0^\circ$	
0.00	1.17	0.00	1.38	0.00	1.20
5.12	74.81	5.36	84.16	0.46	9.19
8.18	124.4	13.56	207.8	2.27	42.75
11.64	176.9	17.37	260.2	3.42	63.09
18.46	274.2	20.57	303.5	7.44	128.8
1.63 ( $\text{H}_2\text{SO}_4$ )	282.5			15.23	239.7
4.73 ( $\text{H}_2\text{SO}_4$ )	294.0	$0^\circ$		$-78.5^\circ$	
8.12 ( $\text{H}_2\text{SO}_4$ )	302.8	0.00	0.78	0.00	0.05
15.77 ( $\text{H}_2\text{SO}_4$ )	313.3	5.36	73.41	0.14	0.41
		13.56	178.9	0.36	1.01
0.00	1.26	17.37	222.8	1.20	3.35
0.89	5.83	20.57	258.5	1.74	4.91
3.49	54.55	$-78.5^\circ$		2.09	5.89
4.60	73.84	0.00	0.06	2.69	7.41
7.47	121.1	1.9	4.08	3.14	8.53
10.19	164.1	4.1	8.97		
15.65	241.4	5.8	12.79	0.00	0.02
2.16 ( $\text{H}_2\text{SO}_4$ )	249.9	7.1	15.50	2.12	5.86
5.61 ( $\text{H}_2\text{SO}_4$ )	259.0	8.5	18.61	2.19	6.04
10.02 ( $\text{H}_2\text{SO}_4$ )	266.0			2.28	6.29
20.35 ( $\text{H}_2\text{SO}_4$ )	273.5			2.41	6.64
30.87 ( $\text{H}_2\text{SO}_4$ )	275.5			2.67	7.36
				4.91	12.83

(1) W. Traube and E. Reubke, *Ber.*, **46B**, 1618 (1921).(2) W. Lange, *Z. Anorg. Allgem. Chem.*, **215**, 321 (1933).(3) R. J. Gillespie and E. A. Robinson, *Can. J. Chem.*, **40**, 644 (1962).(4) R. J. Gillespie, J. B. Milne, and R. C. Thompson, *Inorg. Chem.*, **5**, 468 (1966).(5) J. Barr, R. J. Gillespie, and R. C. Thompson, *ibid.*, **3**, 1149 (1964).

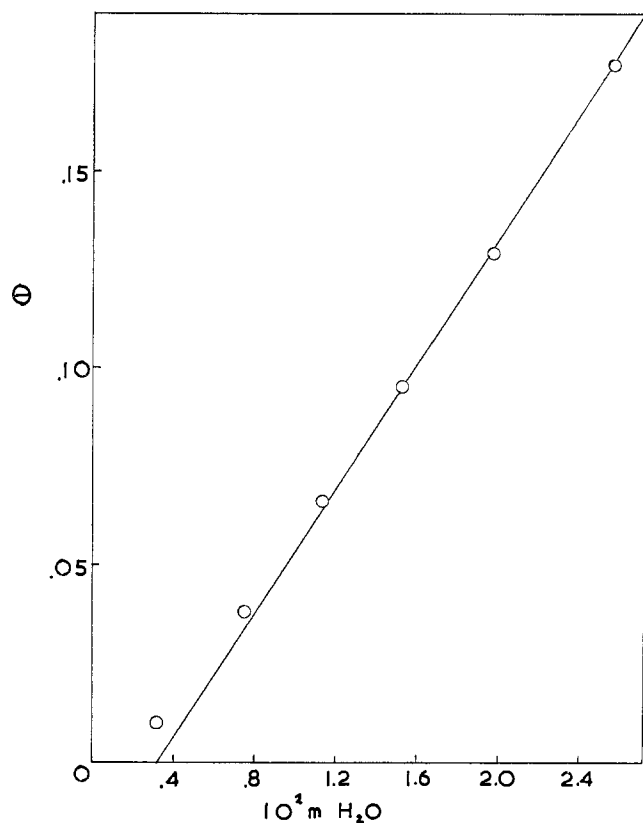
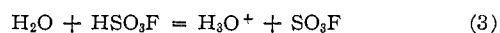


Figure 1.—Freezing-point depression ( $\theta$ ) produced by water. The straight line is a theoretical curve for  $\nu = 2$ .

there is indeed the formation of an equilibrium amount of HF and  $\text{H}_2\text{SO}_4$ . The conductivity curves for water do not pass through the origin because of the initial reaction of the water with the small excess of sulfur trioxide present in the solvent. In each case the amounts of  $\text{SO}_3$  were found by extrapolation of the conductivity curves to be  $0.006\ m$  or less in agreement with the amounts found previously.<sup>4</sup> This initial concentration of  $\text{SO}_3$  was subtracted from the concentration of added water, and then values of  $\gamma$ , the number of moles of fluorosulfate ions produced by 1 mole of solute, were determined by comparison of the concentrations of the water solution and a potassium fluorosulfate solution having the same conductivity.<sup>5</sup> It is assumed that the difference in the mobilities of the  $\text{H}_3\text{O}^+$  and  $\text{K}^+$  ions is negligible.<sup>5</sup> An essentially constant value of  $\gamma$  independent of concentration was obtained at each temperature (Table III). Such a constant value of  $\gamma$  would indeed be expected for equilibrium 1 but not, for example, for the simple ionization of water as a base



For equilibrium 1 we have

$$K_1 = \frac{[\text{HF}][\text{H}_2\text{SO}_4]}{[\text{H}_3\text{O}^+][\text{SO}_3\text{F}^-]} = \frac{(1 - \gamma)^2}{\gamma^2} \quad (4)$$

while for (3) we have

$$K_3 = \frac{[\text{H}_3\text{O}^+][\text{SO}_3\text{F}^-]}{[\text{H}_2\text{O}]} = \frac{\gamma^2 m_{\text{H}_2\text{O}}}{1 - \gamma} \quad (5)$$

Values of  $K_3$  vary over a wide range whereas the values of  $K_1$  are essentially constant. The equilibrium

constant  $K_1$  has a mean value of 0.12 at  $25^\circ$  and appears to decrease slightly with decreasing temperature (Table III).

Addition of sulfuric acid to a solution of water should shift equilibrium 1 back to the left and thereby increase the conductivity. This was found to be the case as shown in Figure 2 and Table II, the increase being much greater than could be attributed to the simple ionization of  $\text{H}_2\text{SO}_4$  as a base.<sup>5</sup> In the presence of additional sulfuric acid the equilibrium constant is given by the expression

$$K_1 = \frac{(1 - \gamma)(1 - \gamma)m_{\text{H}_2\text{O}} + m_{\text{H}_2\text{SO}_4}}{\gamma^2 m_{\text{H}_2\text{O}}} \quad (6)$$

The values calculated from the experimental data and given in Table III are reasonably constant although they are a little higher than the values obtained from solutions of water alone.

The initial curvature of the freezing-point curve for water indicates that equilibrium 2 does not go to completion. Therefore, both HF and  $\text{SO}_3$  must exist together in the solution in finite concentrations. Using the value  $K_1 = 0.031$  and the data in Figure 1, it was found that  $K = [\text{SO}_3][\text{HF}] = 10^{-7}$ – $10^{-8}$  at  $-78^\circ$ . This is consistent with our earlier deductions from cryoscopic studies on the  $\text{SO}_3$ –HF system<sup>4</sup> that  $K < 3 \times 10^{-7}$ .

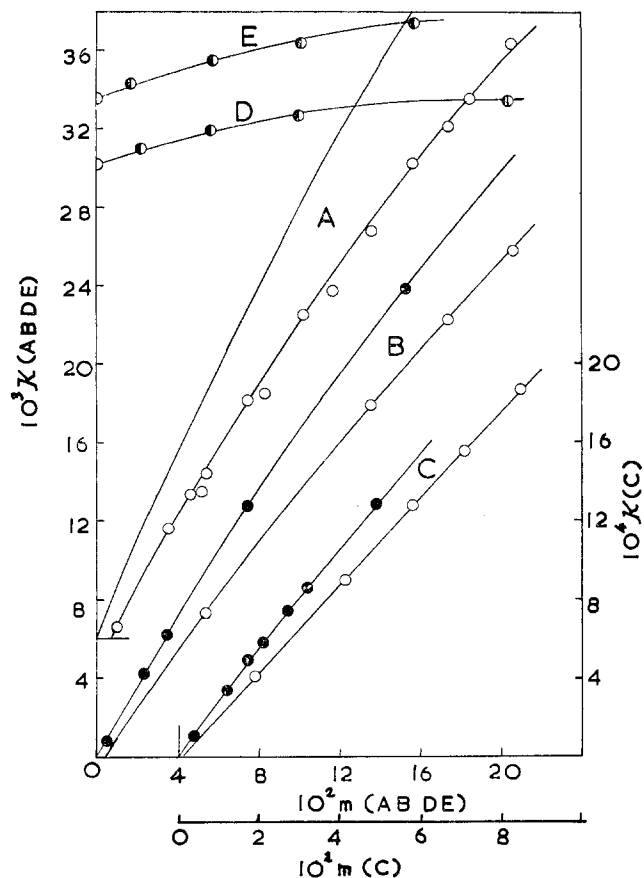


Figure 2.—Conductivities of solutions of water: A,  $25^\circ$ ; B,  $0^\circ$ ; C,  $-75.8^\circ$ ; upper curve ( $\bullet$ ),  $\text{KSO}_3\text{F}$ ; lower curve ( $\circ$ ),  $\text{H}_2\text{O}$ . Experimental points for  $\text{KSO}_3\text{F}$  at  $25^\circ$  are not given (see ref 5). Curves A have been shifted vertically by 6 units and curves C horizontally by 4 units. Curves D and E show the effect of the addition of  $\text{H}_2\text{SO}_4$  on the conductivities of  $0.1846$  and  $0.1565\ m$   $\text{H}_2\text{O}$  solutions at  $25^\circ$ .

TABLE III  
 EQUILIBRIUM CONSTANTS AND  $\gamma$  VALUES FOR WATER

25°				0°		
10 <sup>2m</sup>	$\gamma$	K <sub>1</sub>	K <sub>3</sub>	10 <sup>2m</sup>	$\gamma$	K <sub>1</sub>
6.0	0.75	0.11	0.14	6.0	0.83	0.042
8.0	0.75	0.11	0.19	8.0	0.84	
10.0	0.74	0.12	0.21	10.0	0.83	
12.0	0.74	0.12	0.25	12.0	0.83	
14.0	0.74	0.12	0.29	14.0	0.83	
16.0	0.73	0.14	0.32	16.0	0.84	
18.0	0.73	0.14	0.36	18.0	0.83	

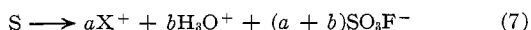
  

-78°				-78°		
10 <sup>2m</sup> H <sub>2</sub> SO <sub>4</sub>	10 <sup>2m</sup> H <sub>2</sub> O	$\gamma$	K <sub>1</sub>	10 <sup>2m</sup>	$\gamma$	K <sub>1</sub>
0.0	18.5	0.73	0.14	2.0	0.84	0.031
4.0	18.5	0.77	0.19	3.0	0.85	
8.0	18.5	0.80	0.20	4.0	0.85	
12.0	18.5	0.83	0.20	5.0	0.87	
16.0	18.5	0.85	0.22	6.0	0.87	

10 <sup>2m</sup> H <sub>2</sub> SO <sub>4</sub>	10 <sup>2m</sup> H <sub>2</sub> O	$\gamma$	K <sub>1</sub>
0.0	15.65	0.75	0.11
4.0	15.65	0.80	0.15
8.0	15.65	0.83	0.16
12.0	15.65	0.86	0.18
16.0	15.65	0.87	0.21

**Complex Electrolytes.**—The above conclusions concerning the formation of HF and H<sub>2</sub>SO<sub>4</sub> in solutions of water mean that this must be allowed for in the interpretation of the  $\gamma$  values of any electrolytes that produce water in their ionization in fluorosulfuric acid. No allowance is needed in the cryoscopic measurements since the equilibrium does not involve any change in the total number of solute particles which remains constant at 2. Consider a solute S which ionizes according to the equation



where  $a$  is the total number of moles of all cations other than H<sub>3</sub>O<sup>+</sup> produced by 1 mole of S. The ions H<sub>3</sub>O<sup>+</sup> and SO<sub>3</sub>F<sup>-</sup> will be in equilibrium with H<sub>2</sub>SO<sub>4</sub> and HF according to eq 1. Suppose that of the  $b$  moles of H<sub>3</sub>O<sup>+</sup>  $x$  moles react to produce H<sub>2</sub>SO<sub>4</sub> and HF. Then

$$K_1 = \frac{[H_2SO_4][HF]}{[H_3O^+][SO_3F^-]} = \frac{x^2}{(b-x)(a+b-x)} \quad (8)$$

This equation can be solved for  $x$  and then  $\gamma = a + b - x$ .

**Potassium Nitrate.**—The above method of obtaining theoretical  $\gamma$  values for complex electrolytes was tested with potassium nitrate. A Raman spectrum of a solution of potassium nitrate in fluorosulfuric acid showed in addition to the well-known lines of H<sub>2</sub>SO<sub>4</sub>, HSO<sub>3</sub>F, and SO<sub>3</sub>F<sup>-</sup> a strong sharp line at 1408 cm<sup>-1</sup> which can be attributed only to the nitronium ion.<sup>6,7</sup>

(6) R. J. Gillespie and E. A. Robinson, *Can. J. Chem.*, **40**, 644 (1962).

(7) C. K. Ingold, D. J. Millen, and H. G. Poole, *J. Chem. Soc.*, 2576 (1950).

Thus, we conclude that nitric acid ionizes in fluorosulfuric acid in an analogous manner to its ionization in sulfuric acid, *i.e.*



The salt nitronium fluorosulfate NO<sub>2</sub><sup>+</sup>·SO<sub>3</sub>F<sup>-</sup> has previously been prepared by the reaction of N<sub>2</sub>O<sub>5</sub> with HSO<sub>3</sub>F in solution in nitromethane.<sup>8</sup>

Calculation of  $\gamma$  by means of eq 8 using  $K_1 = 0.12$  gives  $\gamma = 2.58$ . Experimental values obtained by comparison with potassium fluorosulfate are given in Table IV; they are in good agreement with the calculated value.

 TABLE IV  
 CONDUCTIVITIES OF SOLUTIONS OF POTASSIUM NITRATE AT 25°

10 <sup>2m</sup>	10 <sup>4</sup> $\kappa$ , ohm <sup>-1</sup> cm <sup>-1</sup>	$\gamma$
0.00	1.74	...
2.098	123.5	2.53
3.738	211.4	2.56
5.348	289.5	2.58

### Experimental Section

The cryoscopic and Raman spectroscopic measurements were carried out as described previously.<sup>4,9</sup> Conductivity measurements at 0 and 25° were carried out as described previously<sup>6</sup> in a thermostated oil bath.<sup>5</sup> To facilitate better comparison of the conductometric and cryoscopic results, conductivity measurements were also made at the sublimation temperature of Dry Ice (-78.5°). A conductivity cell with a long sample inlet tube was placed in a dewar flask and covered up to the inlet cap with finely powdered solid carbon dioxide. A steady temperature was achieved by continuously vaporizing some of the carbon dioxide with a small heater. The temperature was read with a platinum resistance thermometer and was found to vary no more than  $\pm 0.01^\circ$  at constant atmospheric pressure. As the atmospheric pressure varied somewhat during measurements, all of the conductivities were corrected to -78.52°, the sublimation temperature of carbon dioxide at 760 mm. The correction factor was determined from the variation with temperature in the neighborhood of -78.5° of the conductivity of potassium fluorosulfate solutions. The corrections were never larger than 1.5%. Water was added to the cryoscope and conductivity cell in the form of a fairly concentrated solution in fluorosulfuric acid, or from a weighed hypodermic syringe which was inserted below the surface of the fluorosulfuric acid; adhering solvent was wiped off the stainless steel needle with hardened filter paper before reweighing.

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(8) D. R. Goddard, E. D. Hughes, and C. K. Ingold, *ibid.*, 2559 (1950).

(9) R. J. Gillespie and E. A. Robinson, *Can. J. Chem.*, **39**, 2179 (1961).