

### 823. The Effect of Temperature on the Ionization of Hydrofluoric Acid.

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From electrical conductance measurements up to 200°, the equilibrium constants for the equilibria  $\text{HF} \xrightarrow{K_a} \text{H}^+ + \text{F}^-$  and  $\text{F}^- + \text{HF} \xrightarrow{K_1} \text{HF}_2^-$  have been obtained. Temperature has a greater effect on  $K_a$  for hydrofluoric acid than on the ionization constants for other acids involving singly charged ions, such as simple carboxylic acids and phosphoric acid (first ionization). The large temperature effect for hydrofluoric acid may be due to the small size of the fluoride ion, and the decrease at higher temperature in the energy of hydrogen bonding the fluoride ion into the water structure. The values of  $K_1$  show only a slight increase with temperature.

IN connection with studies of the solubility of fluoride minerals in water at high temperatures and of the volatility of fluorine in steam from natural hydrothermal systems, the acid strength of hydrofluoric acid has been determined in water at temperatures up to 200°. Earlier results<sup>1,2</sup> on other acids allow comparison of the effects of temperature on the strengths of acids of different types.

The ionization of hydrofluoric acid in aqueous solution at atmospheric temperatures has been interpreted,<sup>3-5</sup> from conductance and e.m.f. measurements, as involving the equilibria,  $\text{HF} \rightleftharpoons \text{H}^+ + \text{F}^-$  and  $\text{F}^- + \text{HF} \rightleftharpoons \text{HF}_2^-$ . In the present work, conductance measurements were made at up to 200° on 0.01—0.1m hydrofluoric acid and 0.002—0.01m-potassium fluoride, and the results combined with published conductance values for hydrochloric acid and potassium chloride<sup>1</sup> in order to obtain values of the constants,  $K_a = a_{\text{H}^+}a_{\text{F}^-}/a_{\text{HF}}$  and  $K_1 = a_{\text{HF}_2^-}/a_{\text{F}^-}a_{\text{HF}}$ , by a modification of the MacInnes method.<sup>6</sup>  $a$  is the molal activity of a solution species, and, in the equations which follow,  $[\text{X}]$  is the molal concentration of species X,  $\gamma_{\pm}$  is the mean activity coefficient of the anion and cation, and  $m$  is the total molal fluoride concentration  $[\text{HF}] + [\text{F}^-] + 2[\text{HF}_2^-]$ . The activity coefficient of un-ionized hydrogen fluoride was taken as unity. At the low ionic concentrations used,  $\gamma_{\text{HF}_2^-}$  was equated to  $\gamma_{\text{F}^-}$ , and  $\gamma_{\pm}$  values were obtained by calculation as in a previous paper.<sup>1</sup> A parameter  $K^*$  is defined as follows:

$$\begin{aligned} K^* &= [\text{H}^+]^2\gamma_{\pm}^2/(m - [\text{H}^+]) = [\text{H}^+](\text{HF}_2^-) + [\text{F}^-]\gamma_{\pm}^2/([\text{HF}] + (\text{HF}_2^-)) \\ &= K_a(1 + K_1[\text{HF}])/(1 + K_1[\text{F}^-]) \\ &= K_a\{1 + K_1(m - [\text{H}^+] - [\text{HF}_2^-])\}/(1 + K_1[\text{F}^-]) \end{aligned} \quad (1)$$

At each temperature,  $K^*$  was evaluated by obtaining the hydrogen-ion concentration from  $[\text{H}^+] = \Lambda m/\Lambda'$ , where  $\Lambda$  is the molar conductance of the hydrofluoric acid solution, and  $\Lambda'$  the sum of molar conductances of the  $\text{H}^+$  and  $\text{F}^-$  ions ( $\lambda_{\text{H}^+} + \lambda_{\text{F}^-}$ ) at the ionic strength of the weak acid solution.  $\Lambda'$  was obtained by interpolating molar conductance results for hydrochloric acid and potassium chloride and fluoride over the appropriate concentration range at the temperature. (Values of  $\Lambda_{\rho}$  were actually used throughout to save the necessity of repeatedly applying corrections for the water density,  $\rho$ .) Values of  $K^*$  were first plotted against  $(m - [\text{H}^+])$ ,  $(\text{HF}_2^-)$  being small in comparison with this difference, and  $(1 + K_1[\text{F}^-])$  being close to unity. This gave an almost linear graph of slope approximately  $K_aK_1$  and intercept  $K_a$ . From the approximate value obtained for

<sup>1</sup> Ellis, *J.*, 1963, 2299.

<sup>2</sup> Noyes, "The Electrical Conductivity of Aqueous Solutions," Publ. No. 63, Carnegie Institution of Washington, 1907.

<sup>3</sup> Pick, "Nernst's Festschrift," W. Knapp, Halle, 1912, p. 360.

<sup>4</sup> Wooster, *J. Amer. Chem. Soc.*, 1938, **60**, 1609.

<sup>5</sup> Broene and de Vries, *J. Amer. Chem. Soc.*, 1947, **69**, 1644.

<sup>6</sup> MacInnes, *J. Amer. Chem. Soc.*, 1926, **48**, 2068.

$K_1$ , the concentrations of  $\text{HF}_2^-$  and  $\text{F}^-$  ions were calculated and  $K^*$  was then plotted against  $(m - [\text{H}^+] - [\text{HF}_2^-]) / (1 + K_1[\text{F}^-])$  to obtain improved values of  $K_a$  and  $K_1$ . If necessary, this process was repeated to obtain final values of  $K_a$  and  $K_1$ .

In this method an error results in the hydrogen-ion concentration, and thereby in  $K^*$ , as it is assumed in obtaining  $\Lambda'$  that the conductance of anions in the hydrofluoric acid solutions is due entirely to  $\text{F}^-$  ions. Some of the  $\text{F}^-$  ions are replaced by  $\text{HF}_2^-$  ions, and as  $\lambda_{\text{HF}_2^-}$  is  $\sim 83$  compared with  $\lambda_{\text{F}^-}$  of 53 and 25° (see Wooster<sup>4</sup>), the calculated hydrogen-ion concentration will be slightly high. The conductance of the hydrogen ion is, however, much greater than that of the anions, and at the temperatures investigated the ratio of bifluoride ion to total anions ranges from 0.03—0.01 for 0.012m- to 0.20—0.40 for 0.093m-hydrofluoric acid, the higher ratios being at the higher temperatures. The errors caused in this way in the values of  $K_a$ , obtained by extrapolation to zero acid concentration, are negligible. At 25° the individual hydrogen-ion concentrations may be high by  $\sim 0.3\%$  for 0.01m- and 2% for 0.1m-acid. At higher temperatures the differences between the mobilities of ions of equal charge diminishes, but the excess conductance of the hydrogen ion also decreases.<sup>7</sup> By equating the temperature effects for  $\lambda_{\text{HF}_2^-}$  to those for  $\lambda_{\text{Cl}^-}$  and assuming  $\lambda_{\text{K}^+}$  is equal to  $\lambda_{\text{Cl}^-}$  it was estimated that the hydrogen-ion concentrations at 200° were too high by amounts ranging from 0.5% at 0.01m- to 2% at 0.1m-hydrofluoric acid. At a particular hydrogen fluoride concentration, this error does not vary much with temperature, and at each temperature the line of slope  $K_a K_1$  was adjusted so that the  $K^*$  value at 0.093m-acid fell 4% below the value that would be given by the mean line through the  $K^*$  values of Table 3.

#### EXPERIMENTAL

*Apparatus.*—The platinum-lined conductance cell described previously<sup>1</sup> was used again, the only modification being substitution of a short Teflon cylinder for the quartz insulator.

*Method.*—In duplicate runs measurements were made at 25° intervals between 25° and 200° at ascending temperatures, and from 200° to 100° on the descending half of the temperature cycle. Good agreement was obtained between runs, and hysteresis effects over the temperature cycle were small and of the same order as reported previously.<sup>1</sup>

The volatility of hydrofluoric acid in the steam phase was investigated by analysing the condensate from a separate half-filled pressure vessel containing a hydrofluoric acid solution of known concentration. The weight concentration of hydrofluoric acid contained in the steam increased with temperature, but at 200°, under the conditions used in the conductance cell, less than 0.1% of the acid in the cell would be present in the vapour phase. The weight concentration of total fluoride in the liquid in the cell during a conductance run would thus be almost independent of temperature.

The removal of the quartz insulator caused lower values to be obtained for the conductance of distilled water (Table 1). The present values are now similar to those reported by Noyes.<sup>2</sup> Adsorption of ions on the porous silica surface, or interaction between the quartz and Teflon, may have caused the slightly higher conductance blanks obtained in the earlier experiments.<sup>1</sup>

The distilled-water blank amounted to a maximum of 2% of the measured conductances at 200° for the 0.01m-acid and was equal to 0.6% for the 0.002m-potassium fluoride at 200°. The contaminating ions in the water would be partly due to carbon dioxide, but are otherwise uncertain. No correction was made to either the acid or the salt conductance for the water blank, but this is unlikely to have introduced errors greater than 1% into the 200° conductance results and much less for those at lower temperatures.

#### RESULTS

Table 1 gives the specific conductance results for the water used in the solutions and, for comparison, those obtained by Noyes.<sup>2</sup>

Table 2 gives the mean conductance results for potassium fluoride solutions. The overall accuracy is likely to be about  $\pm 1-2\%$ . Hydrolysis of fluoride ions to free acid and hydroxide ions would amount to  $>1\%$  for the most dilute solution at 200° and was neglected.

<sup>7</sup> Ellis and Fyfe, *Rev. Pure Appl. Chem. (Australia)*, 1957, **7**, 261.

TABLE 1.

Specific conductance ( $10^6 \text{ ohm}^{-1} \text{ cm.}^{-1}$ ) of distilled water.

		25°	50°	100°	150°	200°
Specific cond.:	present .....	1.05	1.8	3.3	4.9	6.9
	Noyes <sup>2</sup> .....	1.05	1.6	2.9	4.3	5.8

TABLE 2.

Values of  $\Lambda\rho$  for potassium fluoride solutions at various temperatures.

Concn. (m)	25°	50°	75°	100°	125°	150°	175°	200°
0.002	125	193	266	337	408	475	535	590
0.005	123	186	260	330	399	462	522	574
0.01	120	183	252	322	386	444	499	548

The measured values of  $\Lambda\rho$  up to 200° for hydrofluoric acid solutions and associated quantities are given in Table 3, where  $y = (m - [\text{H}^+] - [\text{HF}_2^-]) / (1 + K_1[\text{F}^-])$  obtained by successive approximation. Table 4 summarises the values of  $K_a$  obtained by extrapolating the graph of  $K^*$  against  $y$  to  $y = 0$ , and the values of  $K_1$  derived from the slope of this graph. The measured slopes were decreased by the small amount required by the discussion above.

TABLE 3.

The conductance of hydrofluoric acid solutions, and the derived values of  $K^*$  and of  $y$  (see text).

Temp.	$\Lambda\rho$	$\Lambda'\rho$	$\gamma_{\pm}^2$	$10^4 K^*$	$y$	Temp.	$\Lambda\rho$	$\Lambda'\rho$	$\gamma_{\pm}^2$	$10^4 K^*$	$y$
						0.0930m-HF					
25°	39.5	390	0.823	8.72	0.0798	25°	60.1	394	0.867	7.20	0.0248
50	42.4	523	0.830	5.50	0.0820	50	64.5	530	0.872	4.45	0.0258
75	41.5	655	0.838	3.34	0.0840	75	63.0	662	0.881	2.67	0.0266
100	37.5	748	0.846	2.08	0.0858	100	57.5	755	0.885	1.68	0.0273
125	32.0	831	0.852	1.22	0.0876	125	49.1	840	0.891	0.975	0.0281
150	26.4	892	0.859	0.721	0.0885	150	39.7	902	0.897	0.550	0.0285
175	20.8	934	0.866	0.409	0.0896	175	31.0	944	0.903	0.304	0.0288
200	16.3	971	0.870	0.232	0.0902	200	23.5	980	0.908	0.162	0.0291
						0.0540m-HF					
25	47.9	391	0.845	7.80	0.0456	25	89.0	397	0.894	7.00	0.0092
50	51.5	527	0.851	4.88	0.0470	50	95.0	533	0.900	4.21	0.0097
75	49.5	659	0.862	2.84	0.0488	75	91.8	666	0.906	2.42	0.0102
100	44.5	752	0.868	1.75	0.0496	100	83.2	759	0.910	1.48	0.0106
125	38.0	836	0.874	1.02	0.0505	125	71.4	845	0.915	0.865	0.0110
150	31.2	898	0.881	0.595	0.0514	150	58.6	906	0.920	0.496	0.0112
175	25.1	939	0.886	0.351	0.0519	175	45.8	947	0.924	0.274	0.0115
200	19.6	976	0.890	0.199	0.0523	200	34.2	985	0.930	0.140	0.0114
						0.012m-HF					
25	47.9	391	0.845	7.80	0.0456	25	89.0	397	0.894	7.00	0.0092
50	51.5	527	0.851	4.88	0.0470	50	95.0	533	0.900	4.21	0.0097
75	49.5	659	0.862	2.84	0.0488	75	91.8	666	0.906	2.42	0.0102
100	44.5	752	0.868	1.75	0.0496	100	83.2	759	0.910	1.48	0.0106
125	38.0	836	0.874	1.02	0.0505	125	71.4	845	0.915	0.865	0.0110
150	31.2	898	0.881	0.595	0.0514	150	58.6	906	0.920	0.496	0.0112
175	25.1	939	0.886	0.351	0.0519	175	45.8	947	0.924	0.274	0.0115
200	19.6	976	0.890	0.199	0.0523	200	34.2	985	0.930	0.140	0.0114

TABLE 4.

Values of  $K_a$  and  $K_1$ , and calculated values of  $K_a$ .

Temp. (°C)	25	50	75	100	125	150	175	200
$10^4 K_a$	6.60	4.0	2.3	1.40	0.82	0.46	0.26	0.13
	$\pm 0.15$	$\pm 0.1$	$\pm 0.1$	$\pm 0.05$	$\pm 0.03$	$\pm 0.03$	$\pm 0.02$	$\pm 0.01$
$10^4 K_a$ from eqn. (2)	6.47	4.02	2.42	1.40	0.80	0.44	0.24	0.129
$K_1$	3.4	4.0	4.7	4.8	4.9	5.7	5.8	8
	$\pm 0.5$	$\pm 1.0$	$\pm 0.8$	$\pm 0.8$	$\pm 0.8$	$\pm 1.5$	$\pm 1.5$	$\pm 2$

An estimate of the possible errors (apart from the negligible one in  $m$  since the acid solutions were made by weight in Polythene containers from one stock solution) is given for the 200° results. As noted above, the values of  $K^*$  are slightly too high, owing to the method of obtaining the hydrogen-ion concentration, by amounts which increase with the acid concentration, up to about 4% at 0.093m-acid. Apart from this error, the values of  $K^*$  at 200° for the 0.093m-acid are considered to be accurate to about  $\pm 4\%$ , the possible errors comprising  $\pm 2\%$  due to uncertainties in  $\Lambda\rho$ ,  $\pm 1.5\%$  due to  $\Lambda'\rho$ , and  $0.5\%$  due to the uncertainties in the water

blank. For the 0.0121m-solution the possible error at 200° is considered to be about  $\pm 6.5\%$ , this consisting of  $\pm 3\%$  in  $\Lambda_p$ ,  $\pm 1.5\%$  in  $\Lambda'_p$ , and  $\pm 2\%$  due to the water blank.

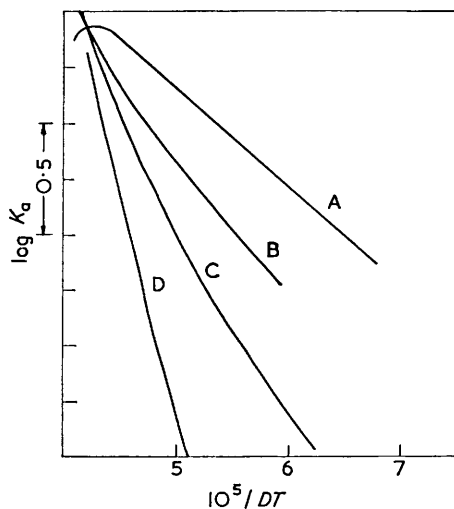
## DISCUSSION

The value obtained for  $K_a$  at 25° is in good agreement with values of 6.89 and 6.71 obtained by Wooster<sup>4</sup> from conductance measurements, and Broene and de Vries<sup>5</sup> from e.m.f. measurements, respectively. The present value of 3.4 for  $K_1$  at 25° may be compared with values of 3.12 and 3.86 obtained in these two earlier investigations. Wooster reported that  $K_a$  was 10.95 at 0°, and this value was used together with the present results in drawing the annexed Figure.

The following equation fits the present results for  $K_a$ :

$$\log K_a = -2.75 - (295/T) + 1.91 \log T - 0.014T. \quad (2)$$

The derived values of the thermodynamic functions at 25°, with limits of significance, are:  $\Delta H^\circ = -3210 \pm 100$  cal. mole<sup>-1</sup>,  $\Delta S^\circ = -25.3 \pm 0.5$  e.u., and  $\Delta C_p^\circ = -34.5 \pm 2$



Comparison of the effects of temperature on the ionization of (A) acetic acid, (B) phosphoric acid (first dissociation), (C) hydrofluoric acid, and (D) sulphuric acid (second dissociation).

cal. mole<sup>-1</sup> deg.<sup>-1</sup>. The heat and entropy changes of  $-3180$  cal. mole<sup>-1</sup> and  $-25.2$  e.u., respectively, reported by Hepler, Jolly, and Latimer<sup>8</sup> from calorimetric measurements are in good agreement with the present results.

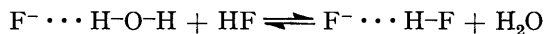
It was shown previously<sup>1</sup> that for a series of carboxylic acids a graph of  $\log K_a$  against  $1/DT$ , where  $D$  is the dielectric constant of water, was almost linear at temperatures  $> \sim 100^\circ$ . In the Figure, the values of  $K_a$  for hydrofluoric acid are plotted against  $1/DT$ , and, for comparison, lines are drawn from results available for acetic acid<sup>1</sup> and the first ionization constant of phosphoric acid,<sup>2</sup> and from tentative results for the second ionization of sulphuric acid.<sup>2</sup> For an ionization involving univalent ions, the effect of temperature is unusually large for hydrofluoric acid. (Note the much larger effect on  $K_a$  for sulphuric acid, where the equilibrium involves a bivalent ion.) The lines for hydrofluoric, phosphoric, and sulphuric acid, are slightly curved and show no sign of the maximum in  $K_a$  below  $100^\circ$  which is found for inorganic oxy-acids such as carbonic,  $H_2PO_4^-$ , boric, and for many carboxylic acids.

As changes in the electrical contribution to the free energy of ionization are predominant at high temperatures,<sup>1</sup> the rapid changes in  $K_a$  for hydrofluoric acid may be due in part

<sup>8</sup> Hepler, Jolly, and Latimer, *J. Amer. Chem. Soc.*, 1953, **75**, 2809.

to the small radius ( $r$ ) of the fluoride ion, as this occurs in the expression  $\log K_a = \log K_e - (Ne^2/9 \cdot 15DrT)$ . It is likely that an additional effect is the change in the energy of hydrogen bonding the fluoride ion into the water structure  $F^- \cdots H-O-H$ . This hydrogen bonding would become less effective at higher temperature, with a consequent decrease in the free energy of ionization of hydrofluoric acid. This explanation suggests that hydrofluoric acid would be a weaker acid at room temperature but for the energy of hydrogen bonding between fluoride ions and water.

Davies<sup>9</sup> showed that the energy of interaction between the fluoride ion and the hydrofluoric acid molecule in the  $(F \cdots H-F)^-$  ion could be explained by electrostatic forces between the HF dipole and the  $F^-$  ion. The present values of  $K_1$  are of low accuracy, but indicate that the proportion of  $HF_2^-$  ion present at a given total acid concentration changes little with temperature, except for a small increase at 200° which appears to be significant. This small change in  $K_1$  with temperature is not unexpected for an exchange reaction involving two hydrogen-bonded ions:



Temperature would have a similar effect on the molecular species on both sides of the equilibrium.

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<sup>9</sup> Davies, *J. Chem. Phys.*, 1947, **15**, 739.

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